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SYNTHESIS AND CHARACTERIZATION OF POLYMERS OF NONANAL, DECANAL, UNDECANAL, AND DODECANAL

A Dissertation Presented

by

JOHN B. STARR, JR.

Submitted to the Graduate School of the
University of Massachusetts in partial
fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

April 1977

Major Subject: Polymer Science and Engineering

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SYNTHESIS AND CHARACTERIZATION OF POLYMERS OF NONANAL, DECANAL, UNDECANAL, AND DODECANAL

A Dissertation

by

JOHN B. STARR, JR.

Approved as to style and content by:

Dr. Otto Vogl, Chairman of Committee

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April 1977

DEDICATION

To my family; especially mother, father, and wife. Without their unwavering support and sacrifice this undertaking could not have been completed.

ACKNOWLEDGEMENTS

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ABSTRACT

Synthesis and Characterization of Polymers
of Nonanal, Decanal, Undecanal, and Dodecanal

John B. Starr, Jr., B.S. Lowell Technological Institute

Directed by: Dr. Otto Vogl

Polymers of nonanal, decanal, and undecanal were prepared and the melting behavior of the polymers was investigated by DSC. The synthesis of the polymers was accomplished in hydrocarbon solvent (especially MCH) with LTB initiator. The yields of the polymers and their inherent viscosities were higher if a cryotachensic polymerization procedure was followed in which the cooling of the polymerization mixture was carefully controlled. The polyaldehydes, which are unstable above their ceiling temperatures, were stabilized by the technique of endcapping of the polymers with acetic anhydride. This technique was useful in the case of polynonanal but was less effective for the higher polyaldehydes. Attempted preparative scale polymerization of dodecanal failed to give isolatable polydodecanal. It was speculated that the physical properties of the polymer adversely affected the monomer - polymer equilibrium and also favoured degradation of the polymer during attempted isolation.

Two transition regions were identified by DSC and optical microscopy for polynonanal (PNA), polydecanal (PDA), and polyundecanal (PUA). When heated to a temperature near or above the upper limit of the first transition the polymers could be extruded.

It was concluded that two types of crystallinity were possible

for PNA, PDA, and PUA. Crystallization of the outer paraffinic side chains gave rise to the first transition of the polymers and crystallization involving the main chains accounted for the second transition; similar to what had been known for polyaldehydes with shorter side chains. The crystallization of the main chains of PUA was less significant than in the case of PNA or PDA. The enthalpies associated with the first transition of the polymers increased as the length of the side chains was increased. Polymer degradation precluded detailed investigation of the second transition region of the polymers.

Aldehyde cyclic trimers (2,4,6-trisubstituted-1,3,5-trioxanes) of nonanal, decanal, undecanal, and dodecanal were prepared. The melting behavior of the trimers was investigated by DSC and compared with that of the polymers. The melting points and heats of fusion of the trimers increased as the length of the alkyl group was increased.

The melting point of the aliphatic aldehyde monomers, purified as for polymerization, was investigated by DSC. The monomers all showed only one transition over the temperature range investigated. The melting points of the trimers were all near or below room temperature.

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CHAPTER I

INTRODUCTION

A. Background

A number of organic compounds of the general structure RCH=X are capable of forming linear polymers via a bond opening chain growth polymerization reaction[1]. In general, polymers from certain of the monomers, where X $=CH_2$, are thoroughly studied and important polymers.

In comparison to the all carbon backbone polymers, polymers from RCH=X monomers with X =O; R =H, alkyl (the aldehyde polymers) have been much less studied. Hereinafter the terms aldehyde polymer and polyaldehyde will be exclusively used to denote the polyaldehydes of reasonable molecular weight formed by the bond opening polymerization of an aldehyde functional group. A clear distinction of nomenclature is necessary since confusion and ambiguity in regards to the use of these terms has arisen in the past[2].

Formaldehyde polymers have been known for some time and early investigation of formaldehyde polymerization[3] led to the development of several basic concepts of polymer science[2]. Continuing research on formaldehyde polymerization led ultimately to development of a commercial material with attractive properties by DuPont[4]. The publication of the "MacDonald" patent has been cited as the beginning of the modern era of aldehyde polymerization[2]. Commercial products based on formaldehyde homopolymers and copolymers of trioxane with ethylene oxide have been developed.

The polymerizations of higher aliphatic aldehydes have been more

recently investigated, although as early as 1929[5, 6, 7] certain higher aliphatic aldehydes (n-butyraldehyde, iso-butyraldehyde, and n-valeraldehyde) were reported to be transformed into viscous oils or waxy solids if the aldehydes were subjected to high pressure (10,000 atm.). These polyaldehydes[8] readily reverted to monomeric aldehyde when allowed to stand at room temperature. Subsequently a rubbery elastomer was produced when acetaldehyde was allowed to freeze and then melt[9, 10] and the polyacetal structure was established for this product[11, 12]. Higher aliphatic aldehyde polymerization was more systematically studied in the 1950's and initially emphasized the polymerization of acetaldehyde. By 1960 it was established that two decidedly different polymers could be obtained from acetaldehyde depending upon the initiator; one rubbery and elastomeric, the other hard and crystalline[13].

During the course of investigations into the preparation of crystalline polyacetaldehyde it was early recognized that higher members of the aliphatic aldehyde homologous series (e.g. butyraldehyde, valeraldehyde, heptanal) could also be polymerized to highly crystalline isotactic polymers. The polymerization of aliphatic aldehydes possessing longer n-alkyl side chains (e.g. hexanal, heptanal, octanal) showed unusual behavior and were recently more critically investigated. It has been noted[14] that, as the alkyl chain length of the aliphatic aldehydes is increased to six carbon atoms (heptanal), the polymerization of acetaldehyde becomes unsuitable as a model for the discussion of higher aliphatic aldehyde polymerization and higher aliphatic aldehyde polymers. As one increases through the aliphatic aldehyde homologous series the paraffinic chain of the aldehyde monomer

more and more influences the polymerization.

The original investigations which described the polymerization of higher aliphatic aldehydes indicated that certain of the higher aliphatic aldehydes yielded polymers which exhibited a transition below the melting point of the polymer. This transition was speculated as arising from "melting" of the paraffinic side chains of the polymers[15]. More recent investigations have confirmed the existence of this "dual-melting" behavior in polymers of aliphatic aldehydes having an n-alkyl side chain of at least 4 carbon atoms[14, 16]. Increasing the length of the alkyl groups of aliphatic aldehydes influenced not only their polymerization but also the properties of the resulting polymers.

B. Polymerization of Aliphatic Aldehydes, Properties and Structures of the Polymers

1. General considerations. The polymerization of formaldehyde and the polymerization of higher aliphatic aldehydes have a number of significant differences which suggest that the polymerization of formaldehyde should be treated separately from the polymerization of acetaldehyde and other higher aliphatic aldehydes.

The polymerization of aliphatic aldehydes proceeds via an ionic mechanism; both cationic and anionic initiation have been used. In general, stronger electrophiles and nucleophiles are required for the polymerization of acetaldehyde and higher aliphatic aldehydes than are required for the polymerization of formaldehyde. The electron-releasing tendency of the alkyl group causes the electron density on the carbonyl

group of higher aldehydes to be relatively higher and consequently the polarization of the carbonyl group is less pronounced in the case of higher aliphatic aldehydes than in the case of formaldehyde. This difference of polarization is reflected in the carbonyl stretching frequency of the aldehydes. The carbonyl stretching frequency of formaldehyde is 1755 $cm.^{-1}$ whereas this value is lowered to 1725 $cm.^{-1}$ for higher aldehydes in the gas phase[17].

Rubbery elastomeric polyaldehydes of high molecular weight are usually made by cationic polymerizations[13] and the crystalline aldehyde polymers, for example polybutanal, obtained from anionic polymerizations. However, the bulk of the alkyl group of aliphatic aldehydes must also be considered when discussing this sort of stereoregulation during aldehyde and other polymerizations.

Aldehyde polymerization, particularly the polymerization of higher aliphatic aldehydes, is subject to the effect of ceiling temperature[19] as illustrated in equation 1. Strictly defined, the ceiling temperature is that temperature at which the concentration of monomer in equilibrium with polymer is equal to one molar. Accordingly, the ceiling temperature may be related to the enthalpy and entropy of the polymerization process[20].

$$\left(\text{-CH(R)-O-}\right)^{*}_{n} + m\ \text{RCHO} \rightleftharpoons \left(\text{-CH(R)-O-}\right)^{*}_{n+1} + m\text{-}1\ \text{RCHO}$$

Eqn. 1

Nominal estimates for the enthalpy of the aldehyde polymerization reaction are in the region of 5-7 kcal $mole^{-1}$. If a typical value of 25-30 $eu.^{o}K^{-1}$ is assumed for this bond-opening chain growth

polymerization reaction then it can be seen that the ceiling temperature for the aldehyde polymerization is below room temperature. The value for the ceiling temperature of the polymerization of acetaldehyde is not substantially different than that measured for the polymerization of n-butyraldehyde (-16^{o})[17]. Failure to recognize the importance of ceiling temperature in the polymerization of aliphatic aldehydes is, in part, responsible for the relatively later introduction of aldehyde polymerization in polymer chemistry.

In view of the above discussion of the effect of ceiling temperature in the polymerization of aliphatic aldehydes it is not surprising that, unless suitably stabilized, polymers of higher aliphatic aldehydes will readily degrade to monomer at temperatures above the ceiling temperature. The technique of endcapping of the polymers, usually by esterification but also by etherification of the polymer end-groups[21], was the typical procedure employed to stabilize the polymers against degradation by an unzipping mechanism. The success of the capping reaction frequently has been sporadic and depended, among other things, upon the bulk of the side group of the polymer and the extent of swelling of the polymer under the conditions of the reaction[22].

2. Cationic Polymerization of Aliphatic Aldehydes. During the course of investigations of aldehyde polymerization a number of chemical compounds have been found to be initiators for the cationic polymerization of aldehydes. Furthermore, a number of special procedures, which thusfar are known to be exclusively applicable to the polymerization of acetaldehyde, have been shown to involve a cationic mechanism. The most important initiators for cationic aldehyde

polymerization can be conveniently grouped into three categories; the Bronstead or protic acids, Lewis acids and their complexes, and certain metal oxides and sulphates.

Under certain conditions the formation of aldehyde cyclic trimer or tetramer is a serious competing or side reaction during the cationic polymerization of aliphatic aldehydes. The problem of cyclic trimer formation is most significant in the case of the lower members of the aliphatic aldehyde homologous series and was found to be particularly acute in the cationic polymerization of acetaldehyde.

The predisposition to trimer formation during the polymerization of acetaldehyde in ether solvent has been used to rate the activity of various Bronstead and Lewis acids as cationic initiators for acetaldehyde polymerization[23]. Normally the cold (-78^{o}C) aldehyde was added to the initiator (0.1 wt%)/solvent mixture at an initial reaction temperature of -78^{o}C. Very active initiators (e.g. H_2SO_4, P_2O_5, $BF_3 \cdot Et_2O$, $FeCl_3$, aluminum sulphate) resulted only in the formation of the cyclic trimer paraldehyde, typically in quantitative yield. Moderately active initiators (e.g. H_3PO_4, HCl, HNO_3, SbF_3, $AlCl_3$) caused polymer formation in high yield at temperatures of -60^{o}C to -80^{o}C. Inactive compounds (e.g. acetic acid, chloracetic acid, ALF_3, $TiCL_2$) gave no detectable amount of polymer at -60^{o}C in ether solvent. The apparent initiator activity was found to have some dependency upon concentration. However, even at concentrations as low as 0.02 wt%, initiators such as BF_3, $SnCl_4$, and some others caused exclusively the formation of paraldehyde at -65^{o}C in ether solvent.

With proper choice of solvent and monomer concentration certain

of the "highly active" initiators were successfully employed for the preparation of high molecular weight polyacetaldehyde in good yield by solution techniques. For example, the use of BF_3 as initiator for the cationic polymerization of acetaldehyde at temperatures of -65°C and below gave only paraldehyde when either ether or pentane was used as the solvent. If, on the other hand, ethylene was used as the solvent when BF_3 was the initiator, a good yield of high molecular weight polyacetaldehyde was realized.

It is interesting to note that there is an early suggestion of a BF_3 initiated cationic polymerization of acetaldehyde in a 1942 patent by Smyers[24]. The structure of polyvinylalcohol was originally assigned to the product by Smyers. However, it appears that the polymer reported in the patent was indeed the polyacetaldehyde.

The effect of concentration on apparent initiator activity was conveniently demonstrated by the polymerization of acetaldehyde with aluminum sulfate (a very active initiator if diethyl ether is the solvent) at -60°C in toluene (0.5% initiator). As the initial concentration of acetaldehyde was reduced from 100% to 50% (in toluene) the product composition changed from strictly paraldehyde in neat acetaldehyde, to only polymer with no trimer at acetaldehyde concentration of less than 50%[23].

Thus the intricate interplay between initiator activity, nature of the solvent, monomer and initiator concentration, and initial reaction temperature controls the effective reaction temperature and hence the formation of high polymer vs. cyclic trimer.

Certain of the techniques and procedures for the cationic

polymerization of acetaldehyde have been used for the polymerization of its higher homologues. For example, both $BF_3 \cdot Et_2O$ and $SnBr_4$ were reported to be effective initiators for the solution polymerization of n-butyraldehyde. Likewise, heptanal has been polymerized with $BF_3 \cdot Et_2O$ in methylcyclohexane solution and gave a white rubbery polymer[22]. The polyaldehydes prepared by a cationic mechanism tend to be more soluble and amorphous in character than the products formed in the anionic polymerization reaction to be discussed later. However, the bulk of the alkyl group and the miscibility of the reactants and solvent at the reaction temperature must be taken into account as contributing factors.

If the polymerization of acetaldehyde with $BF_3 \cdot Et_2O$ was carried out in ethylene as the solvent and the initiator precipitated before the introduction of monomer, a small amount of crystalline, insoluble polymer was isolated in addition to the usual soluble polymer[23]. The product from the $SnBr_4$ initiated polymerization of n-butyraldehyde in pentane solvent was reported to consist of a mixture of insoluble, crystalline polymer and fractions of increasingly soluble, less crystalline polymer[25].

The x-ray powder diagram of a sample of polyheptanal, prepared by the $BF_3 \cdot Et_2O$ initiated polymerization of heptanal, indicated that although the polymer was largely amorphous, a modest amount of crystallinity could be detected. Similarly, when a number of aliphatic aldehydes were polymerized by subjecting them to high pressures[26] the crystallinity of the polymer (by x-ray) was greater with increasing lengths of the alkyl group.

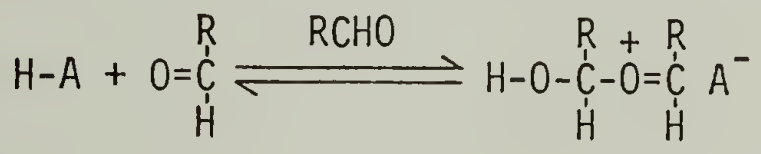
As previously mentioned there are a number of reported procedures for the polymerization of acetaldehyde which thus far have proven to be exclusively applicable to acetaldehyde and are believed to involve a cationic polymerization mechanism. The "crystallization polymerization" of acetaldehyde, discovered by Letort[9] and Travers[10], was originally thought to involve a free radical mechanism and the apparent beneficial effect of oxygen and ultraviolet radiation[27, 28, 29] was taken to support this view. However, further studies[23, 30, 31] showed that crystallization polymerization is but another example of the cationic polymerization of acetaldehyde.

Other techniques for the polymerization of acetaldehyde to the elastomeric polymer use solid state initiators, which are immiscible with monomeric acetaldehyde and any dilutents employed, and are believed to involve a cationic polymerization mechanism. Furukawa and collaborators converted acetaldehyde to a non-tacky elastic solid by condensing the aldehyde at low pressure (3mm. Hg) and low temperature ($-70^{o}C$) onto alumina which had been carefully calcined at 500-$600^{o}C$ for 15 hrs.[82]. Subsequent more detailed studies indicated that a cationic polymerization mechanism was probably involved and that electron deficient sites on the alumina surface were important in the process[33, 34, 35]. Silica, silica-alumina, and other metal oxides are also reported to polymerize acetaldehyde in a similar manner[36, 37]. If properly pretreated with acids certain metal salts, especially metal sulfates, also initiate the polymerization of acetaldehyde to the soluble, elastomeric polymer[38].

Aluminum alkyls, especially $AlEt_3$, were found to be initiators for

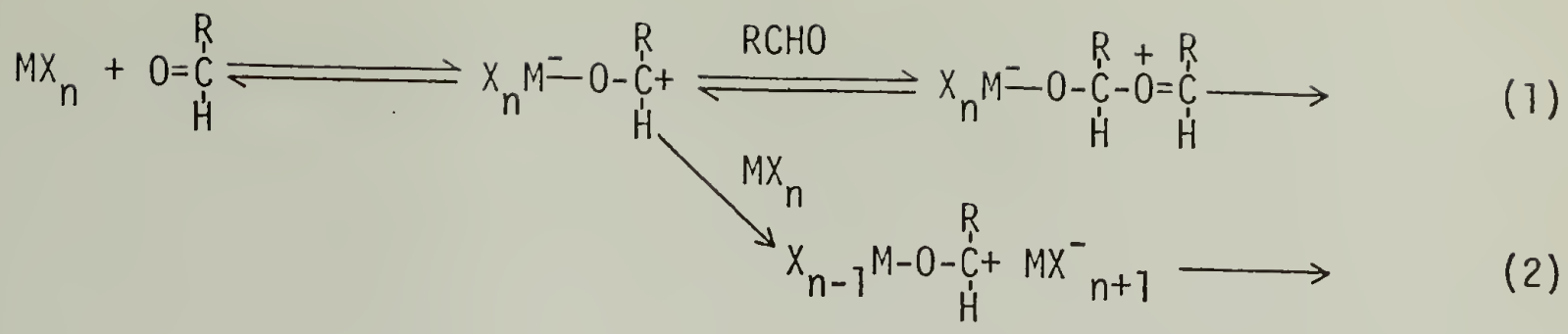
the polymerization of aliphatic aldehydes[39, 40]. The nature of the polymerization mechanism apparently operative in the $AlEt_3$ initiated polymerization of acetaldehyde is strongly dependent upon the reaction conditions[41], i.e. these initiators are considered to be "amphoteric"[17]. The nature of the polymerization reaction and the type of polymer formed with aluminum alkyl initiators seemed also to be dependent upon the type and amount of deliberately added or fortuitously present "impurities", especially protic material[35, 41]. Dialkyl aluminum chlorides also initiate the polymerization of aliphatic aldehydes[42, 43], apparently by a cationic mechanism.

The mechanism of the cationic polymerization of aliphatic aldehydes when protic acid is the initiator may be considered in a straightforward manner Equation 2. Electrophilic attack at the carbonyl oxygen of the aldehyde monomer further decreases the electron density at the carbonyl carbon. Propagation proceeds by attack of the carbonyl oxygen of the monomer at the electrophilic carbon atom adjacent to the oxonium ion. An oxionium ion is now considered to be the chain carrier, similar to the mechanism of cyclic ether polymerization[17, 42].



Eqn. 2

The mechanism with Lewis acid initiators is much more difficult to explain and is much less well understood. Induction periods are normally observed with these initiators. Addition of the Lewis acid (MX_n) at the carbonyl could be followed by at least two reaction paths, Equation 3.



Eqn. 3

In the first reaction scheme, 1, the addition of the Lewis acid is followed by attack at the electrophilic carbon atom by the oxygen atom of the aldehyde monomer to form a new electrophilic center with propagation continuing in a similar manner. This mechanism would require an increasing degree of charge separation unless some sort of head-to-tail arrangement of the growing polymer chains is assumed.

Rearrangement of the initial adduct followed by reaction of the rearranged adduct with a second molecule of Lewis acid to form a carbenium ion complex salt, 2, has been speculated to explain the initiation when BF_3 is the Lewis acid[43]. However, there is no supportive experimental evidence. The monomeric aldehyde could then react with the complex to form an initiated chain with propagation occurring in the usual way with a definite gegenion.

Very little is known about the occurrence of chain transfer during the cationic polymerization of aliphatic aldehydes. The very high molecular weights achievable in the cationic polymerization of acetaldehyde[23] suggest that chain transfer reactions, if they occur, do not efficiently compete with the propagation reaction.

3. Anionic polymerization of aliphatic aldehydes. A large number of compounds, which belong to a variety of chemical classifications, have been identified as initiators for the low temperature anionic

polymerization of aliphatic aldehydes. The polymers obtained from the anionic polymerization of aliphatic aldehydes are quite insoluble and much more crystalline than the products from the cationic polymerization[44]. The mechanism of polymerization of aliphatic aldehydes to soluble, less crystalline polymers with phosphine initiators[45] has yet to be established. Also, the length of the side chain must again be considered. Under certain typical conditions of the anionic polymerization, acetaldehyde yields a polymer of which 50-60% is insoluble in common organic solvents at room temperature[25]. The insoluble fraction of the polymer from the anionic polymerization of n-butyraldehyde or heptanal is much greater, heptanal giving an essentially completely crystalline polymer product.

As previously mentioned, relatively stronger nucleophiles are needed for the polymerization of higher aliphatic aldehydes as compared to formaldehyde[13]. Alkali alkoxides have been shown to serve well as initiators for the polymerization of acetaldehyde and its higher homologues[25, 44]. According to the overall rate of initiation and polymer formation, the initiator activity of a number of alkali alkoxides increased as the length or chain branching of the alkyl group of the alkoxide was increased. Similarly, triphenyl methoxides were more active initiators for the anionic polymerization of aliphatic aldehydes than were benzoxides.

Alkali alkyls and Grignard reagents have also been reported to be initiators for the polymerization of aliphatic aldehydes. Initiation by either of these classes of compounds can be viewed as alkoxide initiation since these compounds are known to react with an aldehyde at

low temperature to form an alkoxide[46] which would be the actual initiator specie. Similarly, benzophenone ketyls and Na-DMF complex are known to be initiators for higher aliphatic aldehyde polymerization.

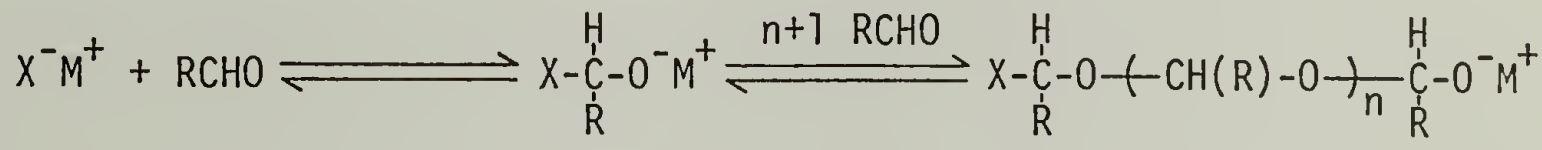
There are several features of the anionic polymerization of aliphatic aldehydes that should be mentioned at this point. First, crystalline polyaldehyde always precipitates from the polymerization mixture during the anionic polymerization reaction. Secondly, once this precipitation occurs, the remaining yet unreacted monomer is not distributed uniformly throughout the polymerization mixture but is absorbed in the precipitated polymer. Furthermore, the extent of swelling of the precipitated polymer by monomer depends upon both the nature of the solvent and the length of the alkyl group of the aliphatic aldehyde.

As mentioned in section B.2., crystalline, insoluble polymers of aliphatic aldehydes have been prepared with aluminum alkyl initiators under properly selected reaction conditions[41, 47]. Although the overall mechanism of the initiation reaction and the nature of the initiating specie with these initiators are not yet well understood, the polymerization may be cationic or anionic in nature depending upon the exact reaction conditions.

Tani[48, 49] has reported the preparation of initiators for the polymerization of aliphatic aldehydes to crystalline insoluble polymers by the reaction of aluminum alkyls, especially $AlEt_3$, with a number of organic compounds, in particular alcohols, amines, or ketones. The initial reaction product is further reacted with a second molar amount of aluminum alkyl to prepare the initiator. Similarly, the reaction

product of triethylaluminum with an N-phenyl acid amide is reported to be an excellent initiator for the polymerization of aliphatic aldehydes to crystalline polymers[50]. High yields of essentially completely crystalline polymers are reported. Despite the detailed investigation of the structure of the initiator and its complexes with aliphatic aldehydes[51, 52] there is still uncertainty concerning the mechanism of action of these initiators.

The generally accepted overall mechanism of the anionic polymerization of aliphatic aldehydes with a variety of initiators can be represented by a direct scheme[17]. Nucleophilic attack by the anionic initiator at the carbonyl carbon of the aldehyde forms a new alkoxide[21, 46]. The alkoxy substituted alkoxide can then propagate by a series of similar attacks, Equation 4. Failure of a given compound to effect the polymerization of aliphatic aldehydes could be due to either the failure of the intended initiator to add at the carbonyl of the monomer and establish a favorable equilibrium or the inability of the products of the initiation reaction to propagate.



Eqn. 4

The propagation reaction, as outlined, proceeds with a specific gegenion. The nature of the gegenion and its interaction with the active chain end is known to play a significant role in the ionic polymerization of many vinyl and diene monomers[53]. The anionic polymerization of aliphatic aldehydes with alkali metal alkoxides and other initiators with different alkali metal cations has been investigated

with n-butyraldehyde as the monomer[25]. Any differences in the results between the polymerizations with various initiators could be accredited to differences in the solubility of the initiators as the identity of the alkali metal was changed. In all cases a highly crystalline polymer with no soluble fraction was obtained[17, 25].

In the initial investigations of the polymerization of higher aliphatic aldehydes no polymers of aldehydes higher than octanal were reported[25]. It was suggested that higher melting aldehydes with longer side chains (e.g. decanal) might not be capable of polymerization by low temperature anionic solution polymerization because the rate of crystallization of monomer from its solution would effectively compete with the rate of polymerization at temperatures near or below the ceiling temperature.

The nature of the solvent is an important factor in the anionic polymerization of aliphatic aldehydes. The low temperature anionic polymerization is best conducted in solvents of low dielectric constant. Solvents with higher dielectric constants have been found to adversely affect the monomer - polymer equilibrium and their use results in a decrease in polymer yield[25]. Although the nature of the gegenion appears to exert little influence in the anionic polymerization of aliphatic aldehydes by alkali metal compounds in solvents of low dielectric constant, solvents with high dielectric constants, which could be expected to promote extensive dissociation of the ionic chain ends (e.g. acetonitrile, DMF), are unsuitable in anionic aldehyde polymerization. At best only trace yields of polymer have been obtained in such solvents[17, 54].

Although ethers in general are poor solvents for the anionic polymerization of aliphatic aldehydes, acetaldehyde may be polymerized with $LiAlH_4$ in ether to give a polymer with a substantial crystalline fraction. Indeed, the first isotactic polyacetaldehyde was prepared with this system in 1958. In this light it is noted with some curiosity that Sumitom[55] has reported that n-valeraldehyde is polymerized in THF with Li-benzophenone complex to give a polymer apparently having much lower crystallinity than the same polymer prepared with alkoxide initiators in solvents such as propylene[25] or methylcyclohexane[22].

The low temperature anionic polymerization of aliphatic aldehydes with most initiators is substantially free of side reactions. Water, carboxcyclic acid, alcohol, or other protic impurities in the solvent or monomer react to consume one equivalent of the anionic initiator. However, n-butyraldehyde contaminated with 1.7 mole% butyric acid was polymerized to 2.5% conversion with 0.15 mole% $K\emptyset_3CO$ initiator at -75^oC in pentane solvent[21]. Incomplete neutralization of the catalyst at the low temperature in the low dielectric constant solvent was cited as the reason for the residual initiator activity.

Chain transfer in anionic polymerization of aliphatic aldehydes has been discussed to a greater extent than for the case of the cationic polymerization. The conversions attainable in the anionic polymerization are comparable to those obtained by the cationic polymerization, however the molecular weights of the anionic polymers tend to be relatively lower. This observation would indicate a greater importance of chain transfer in the anionic polymerization. Effective chain transfer, i.e. cessation of growth of an individual polymer chain but

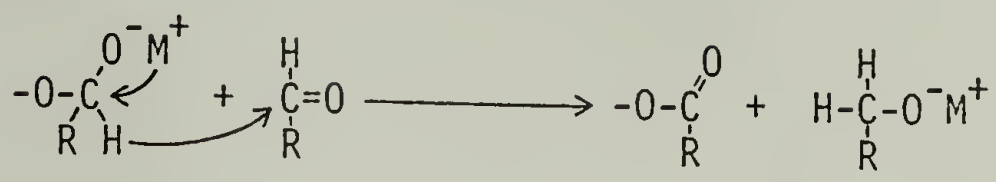
continuation of the kinetic chain, requires that a new anion capable of initiating a new polymer chain be formed in the chain transfer reaction. A number of reactions have been cited as potential chain transfer reactions in the anionic polymerization of aliphatic aldehydes.

Compounds such as those previously mentioned, which possess labile protons and which are not consumed in the embrionic stages of the polymerization reaction, might be expected to function as chain transfer agents. However, depending on their amount and how such agents were introduced into the system, the conversion of monomer to polymer was found to be decreased to a greater or lesser extent in the presence of such compounds but the molecular weight of the polymer was not significantly altered[21].

Chain transfer in anionic aldehyde polymerization might also occur by a proton transfer reaction involving the protons of the carbon atom α to the carbonyl of the aldehyde monomer. The alkoxide anion at the end of a growing polymer chain, acting as a base, could remove an α proton of the aldehyde monomer (or a hydroxyl proton of its enol tautomer) to give a hydroxyl terminated polymer chain and the enolate anion of the aliphatic aldehyde monomer. The aldehyde enolate anion, which is postulated to be the actual initiator in the polymerization of aliphatic aldehydes with alkali metal initiators, could then reinitiate aldehyde polymerization to give a polyaldehyde with one enol ether endgroup[21].

A hydride transfer reaction, similar to that proposed in the mechanism of the Cannizzaro, Tischenko, and related reactions[56], can also be considered as a possible chain transfer reaction, Equation 5.

The alkoxide formed could act to reinitiate a new polymer chain.



Eqn. 5

Such a reaction, in which a polymer chain with one stable ester endgroup is formed directly, could account for the observation that a small (3-6%) fraction of more stable polyaldehyde was isolated if the raw uncapped polymer was degraded in hot tetrahydronapthalene[25].

If great care is taken to suppress the level of impurities in the polymerization mixture the equilibrium anionic polymerization of aliphatic aldehydes may proceed in an unterminated or "living" system[21]. However, as previously mentioned, the crystalline polymer always precipitates during the polymerization reaction and a number of polymer chains become effectively terminated by occlusion of the active end.

4. Chemical structure of the polyaldehydes and stability of the polymer. The polyacetal structure of the polymers formed by the low temperature ionic polymerization of aliphatic aldehydes has now been accepted for all aldehyde polymers prepared by cationic or anionic polymerization. Polymers from the crystallization polymerization of acetaldehyde and high pressure polymerization of higher aliphatic aldehydes are the same and their structure was first suggested[7, 11], by analogy with polyoxymethylene from formaldehyde, on the basis of the facile polymerization-depolymerization reaction and infrared data.

Novak and Whalley reinvestigated the polymerization of higher aliphatic aldehydes at elevated pressures (10 kb.) and evaluated the infrared absorption spectras of the viscous oils or brittle, waxy

solid polymers[8, 26, 57]. Four bands in the region of 1200-800 cm.$^{-1}$ (1132-, 1087-, 1040-, 955-cm.$^{-1}$) were assigned to fundamental skeletal stretching bands of C-O bonds in a polyacetal backbone and the authors reached conclusions similar to those reported by Sutherland[85]. The results of later work with other compounds having the O-C-O-C linkage[58] are in agreement with the assignments made by Novak and Whalley. The infrared spectra of soluble amorphous and insoluble crystalline polyaldehydes prepared by other methods compare favorably with these results.

PMR spectroscopy of soluble polyaldehydes, particularly elastomeric polyacetaldehyde prepared by low temperature solution polymerization with BF_3 initiator, further indicates the polyacetal structure of the polyaldehydes[59]. A fairly broad absorption was recorded near 5.10 δ which could conveniently be assigned to resonance of protons in the structure -O-(R)C<u>H</u>-O-. Such an assignment agrees well with line positions recorded in the spectrum of polyoxymethylene, aldehyde cyclic trimers, and polymers of cyclic formals.

Polyaldehydes degrade easily in acid solution and if this is conducted in the presence of 2,4-dinitrophenylhydrazine a near quantitative yield of the hydrazone of the aliphatic aldehyde monomer results[15]. This observation further confirmed the polyacetal structure.

Polyaldehydes, freshly prepared, are intrinsically thermally unstable. The thermal instability is even more acutely noted in solution[15, 25]. The stability of polyaldehydes can be substantially increased by endcapping of the polymers with more stable groups[21, 25, 60]. In general the polymers are not soluble under the conditions of

the endcapping reaction. Because of this and various other factors the results of the endcapping reactions are not always well reproducable.

Endcapping alone does not always provide ultimate stabilization of the polyaldehydes which are further susceptible to random clevage by acidolysis or by autooxidation. Antioxidants and thermal stabilizers[61] must be added in order to provide ultimate stabilization of polyaldehydes. Samples of polyaldehydes which are well capped and protected with other stabilizers are sufficiently stable so that they may be brought into solution at temperatures of 100°C or above.

5. Stereochemistry of the aldehyde polymerization reaction and the solid state structures of the polymers. The necessity of regularity in macromolecular architecture in terms of both chemical constitution and spatial distribution of atoms is a well known and generally accepted condition in order to achieve crystallinity in high polymers. Head to tail polymers from monomers of the type RCH=X (X =CH_2;O) are capable of existing in two stereoregular configurations which have the requisite regularity and symmetry in the succession of monomer units[62]. Deliberate attempts to prepare stereoregular polymers from aliphatic aldehyde monomers, analogous to those known from vinyl monomers, led to the nearly simultaneous announcement of the preparation of crystalline, presumably stereoregular, polymers from higher aliphatic aldehydes by Vogl[25, 63], Natta[64] and Furukawa[65].

By means of detailed x-ray investigations Natta and coworkers[66] conclusively demonstrated the isotactic structure of the crystalline polymers of the lower members of the aliphatic aldehyde homologous series and have determined their crystal structure. PMR[22] and

x-ray[67, 68] investigations have shown that the crystalline polymer obtained from the anionic polymerization of heptanal is similar in regards to the structure of the backbone chain.

A number of factors must be considered in discussing stereoregulation in the propagation reactions. The structuration of the aliphatic aldehyde molecules in solution at low temperature[69], particularly in the vicinity of the growing chain end, is one factor that is important but is not always considered. Similarly, possible aggregation of the alkali metal gegenion with other initiator molecules, particularly when lithium is the cation, is another factor that does not always receive proper attention. Furthermore, stereoregular polymer always precipitates early in the polymerization reaction and apparently encumbers monomer from its solution. One mechanism for the stereoregular anionic polymerization of aliphatic aldehydes has been proposed in which more than one monomer molecule is involved in the transition state and in which coordination of the oxygen atom of the prepenultimate unit with the gegenion would allow the growth of the polymer chain directly in a helical conformation[70, 71].

The stereoregulation in aldehyde polymerization has been shown to increase as the length of the alkyl group of the aliphatic aldehyde is increased. The detailed interrelation of these various factors in controlling the attainment of a proper rate of polymerization has been suggested to play a critical role in the stereoselectivity of aldehyde polymerizations[21].

Stereoregulation is not as important in the cationic polymerization as in the anionic polymerization and only vanishingly small amounts of

crystalline polyacetaldehyde may be obtained by cationic polymerization under very selected conditions. Somewhat larger proportions of crystalline polymer may be obtained from the cationic polymerization of n-butyraldehyde which has a more bulky n-propyl side group; particularly when halides of heavier metals (e.g. $SnBr_4$) are the initiators.

The tacticity of amorphous elastomeric polyacetaldehyde has been independently investigated by two groups[72, 73] and indeed the polymer was found to possess more than one type of stereochemical sequence in the backbone. Further examinations[60] indicated that elastomeric polyacetaldehyde was largely atactic but did contain a relative excess of isotactic triads.

The crystal structure of the isotactic polymers of certain lower members of the aliphatic aldehyde homologous series, with up to 4 carbon atoms in the side chain, has been determined[66]. More recently[68] the crystal structure of isotactic polyheptanal has also been reported. The isotactic polymers of the lower aldehydes have a helical conformation in the solid state with four monomer units in one turn of the helix. The helices of isotactic polymer pack together in a tetragonal unit cell in which there is four macromolecular chains. The screw sense of the helices alternate within the unit cell such that the nearest neighbors of any one polymer chain have the same helical sense which is opposite to that of the helix in question. The identity period along the helix axis, the c dimension of the unit cell, assumes a constant value of 4.8Å for the polymers of the lower normal aliphatic aldehydes while the remaining dimension of the unit cell (a=b) increases in a regular way. The identity period for polyaldehydes with branched

side chains is slightly greater than the value for the polymers with unbranched sidechains.

The x-ray data from powder patterns and oriented samples of polyheptanal may be interpreted in terms of a model of the crystal structure of the polymer which is very similar to that of polybutanal. Two important differences are noted in comparing the crystal structures of the two polymers. First, the c spacing of crystalline polyheptanal, 4.52Å, is slightly smaller than that of polybutanal, 4.79Å, and second, the polymer chains of polyheptanal are rotated about the helix axis through an angle of ca. 13^{o} with respect to the polymer chains of polybutanal. Both these differences have been related to the packing requirements of the longer alkyl side chains of polyheptanal.

Throughout the preceeding discussions in this chapter the role or influence of the side chain of the aliphatic aldehyde has been referred to in a number of instances. In following discussions even more emphasis will be placed on the effect of the size or bulk of the side chain of the polymer upon various aspects of the chemistry and physical properties of polyaldehydes.

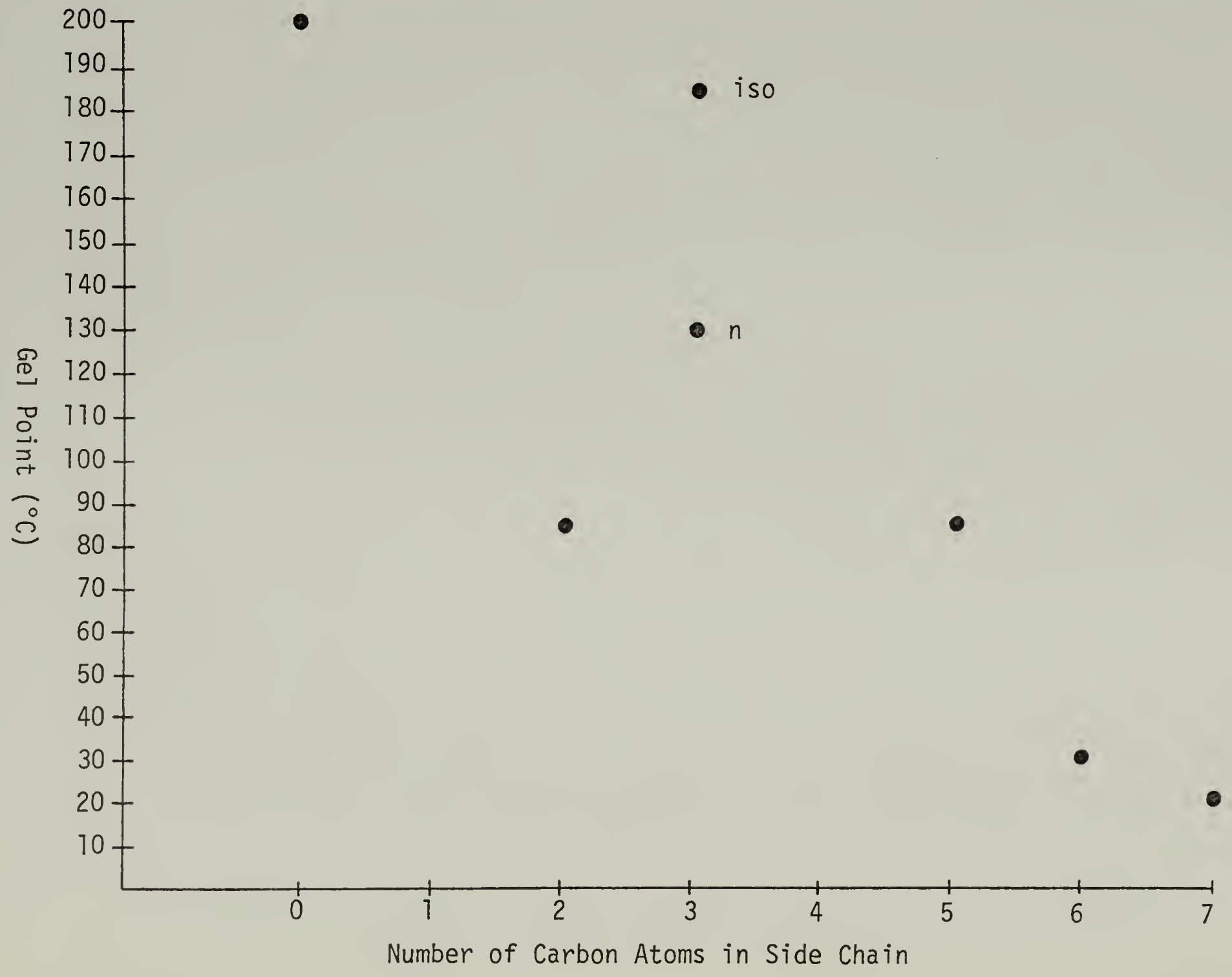
6. Physical properties of aliphatic aldehyde polymers. Certain of the physical properties of a polymer may be influenced by its molecular weight. Molecular weights of 10^{5}-10^{6} may be achieved in the polymerization of acetaldehyde to the amorphous polymer. In general, polymers of relatively lower molecular weight are formed in anionic polymerization of aliphatic aldehydes to crystalline polymers[17]. The crystalline polymers may be sufficiently stabilized to allow the solution viscosities of the polymers to be determined. The inherent

viscosities of 0.5 g./dl. solutions of the stereoregular polymers in tetralin are normally reported to be in the range of 0.35 dl./g., although an inherent viscosity of 0.83 dl./g. for some samples of anionically prepared polybutanal has been reported[25]. The inherent viscosity determined for polymers of higher aliphatic aldehydes with longer side chains (e.g. polyheptanal) may be anomalously higher than that for a polyaldehyde with a shorter side chain prepared under identical conditions[15].

The solubility characteristics of polyaldehydes are notably influenced by the length of the polymer side chain. Gel points of solutions (5% solids) of various polyaldehydes with n-alkyl side chains are given graphically in Figure 1[15]. The value for iso-butyraldehyde is also included. The polymer and solvent were heated to effect solution and then cooled until opalescence was just noted. The polyaldehydes with longer side chains are also affected by a larger number of common organic solvents, at least to the point of limited swelling.

The melting points of the homologous series of polyaldehydes, where the homologous series develops in the side chain, were found to vary with the length and branching of the side chain in much the same manner as was observed in the case of the corresponding olefin polymers. The melting point of the polyaldehyde appeared to increase in passing from polyacetaldehyde (m.p. 165°C, 180°C)[74] to polypropanal (m.p. 185°C) to polybutanal (m.p. 225°C)[15]. The melting point of poly(iso-butyraldehyde) has been estimated to be greater than 260°C but the polymer degraded substantially before melting. The melting point of polypentanal (155°C) is lower than that of polybutanal. When the melting

Figure 1: Gel Points of Crystalline Polyaldehydes (5% Solids in Tetralin)



point of polypentanal was first investigated it was found that a new transition could be observed in the polymer at 85°C, a temperature well below the ultimate melting point of the polymer. Similarly, two transitions were observed for polyheptanal (75°C, 150°C); only one was reported for polyoctanal. The first, lower temperature transitions were speculated as arising from transitions which involved the aliphatic side chains of the polymers[15].

The multiple or dual melting behavior of aliphatic polyaldehydes has more recently been investigated in greater detail and the original speculation that the first melting range reflected transitions which primarily involved the aliphatic side chains has been substantiated[75, 76]. The most detailed work published to date concerning aliphatic aldehyde polymers with longer side chains has emphasized polyheptanal[22].

Two transition regions were clearly identified by a combination of differential scanning calorimety (DSC), thermomechanical analysis (TMA), and optical microscopy in samples of crystalline polypentanal, polyhexanal, polyheptanal, and polyoctanal. When heated to a temperature within or slightly above the first melting range the brittleness of the long side chain polymers decreased markedly and the polymers could be extruded at these temperatures[15, 68]. The effect of thermal and mechanical history on the details of the first, lower temperature transition of several of these polymers has been investigated[77]. The thermal instability of the polymers has precluded the investigation of the melting behavior of polyaldehydes in the temperature region of the second, or ultimate melting transition which involves the backbone chains of the polymer.

The DSC thermograms in the temperature range of the first transition region of the higher aliphatic polyaldehydes normally appeared as a series of endothermic peaks or peaks with shoulders which covered a range of 30-40^{o}C. The favorable comparison of the thermodynamic data, suitably modified[78], for the transitions of the aliphatic polyaldehydes in the first melting region with literature data for the fusion of n-paraffins gave further support to the concept of side chain crystallization in these polymers. The occurrence of recrystallization or reorganizational phenomena associated with the first, or side chain, melting of polyaldehydes with 4 or more carbon atoms in the side chain was also indicated[68]. The transitions in the first melting region of polyheptanal were significantly suppressed by thermomechanical treatment, such as extrusion, which introduces considerable orientation into the still highly crystalline polymer.

Thermal and x-ray investigations on polyaldehydes indicated that, at least up to polyoctanal, both the backbone and less polar paraffinic side chains contribute in a number of ways to determining the structure and properties of the polymers. It is reasonable to assume that the relative importance of the main and side chains in influencing the melting behavior and structure of the polymers will shift more and more to the paraffinic side chains in polyaldehydes with still longer side chains.

7. Copolymers of aliphatic aldehydes. A number of copolymers of aliphatic aldehydes have been reported. In many instances results were reported for unrefined or unfractionated copolymerization products and hence there is substantial doubt as to the composition of the product

and extent of copolymerization.

Elastomeric polyacetals with variable physical and mechanical properties were reportedly obtained by the copolymerization of acetaldehyde and formaldehyde[79, 80]. With BF_3 as the initiator acetaldehyde was copolymerized with up to 15% of an aliphatic aldehyde comonomer, including normal and iso-valeraldehydes. Aldehydes having multiple bonds, aromatic structures, or other functional groups conjugated with the aldehyde carbonyl, which do not form homopolyaldehydes, are reportedly unreactive in copolymerization[81, 82].

Of greater interest to discussions in this thesis are reports concerning crystalline binary copolymers of various members of the higher aliphatic aldehyde homologous series. Various pairs of the aliphatic aldehydes; acetaldehyde/propionaldehyde, and acetaldehyde/butyraldehyde were copolymerized with an Et_3Al - diphenylacetamide catalyst. The c lattice spacing of the crystalline copolymers was invariant while the a spacing was claimed to vary linearly with copolymer composition. The crystal structure of the homopolymers are known to be very similar and the data from the copolymers was taken to indicate an isomorphism of monomer units in the crystalline copolymers[83]. The x-ray diffraction diagrams of n-butyraldehyde / n-heptaldehyde copolymers also showed a variation with comonomer content. The product of the 7:3 copolymerization originally showed no reflections at $2\theta<12^{o}$, however, strong reflections were observed in this region if the copolymer was annealed.

Copolymers of aliphatic aldehydes with isocyanates[84, 85] and with aldehydes having various functionalities in the side group have also

been reported.

C. Other Aldehyde Polymers

The polymerization of several substituted aldehydes, besides branched aliphatic aldehydes, such as phenylacetaldehyde and cyclohexaldehyde was reported at the same time the polymerization of aliphatic aldehydes was reported in greater detail[25]. The polymerization of aliphatic aldehydes having alkylthio substituents has also been reported[86, 87] and the kinetics and mechanism of the polymerization of these monomers with aluminum alkyl initiators has been studied[88]. The polymerization of a number of alkoxy substituted aldehydes[89, 90], as well as cyano, acetoxy, and carbomethoxy substituted propionaldehydes[91, 92] has likewise been investigated.

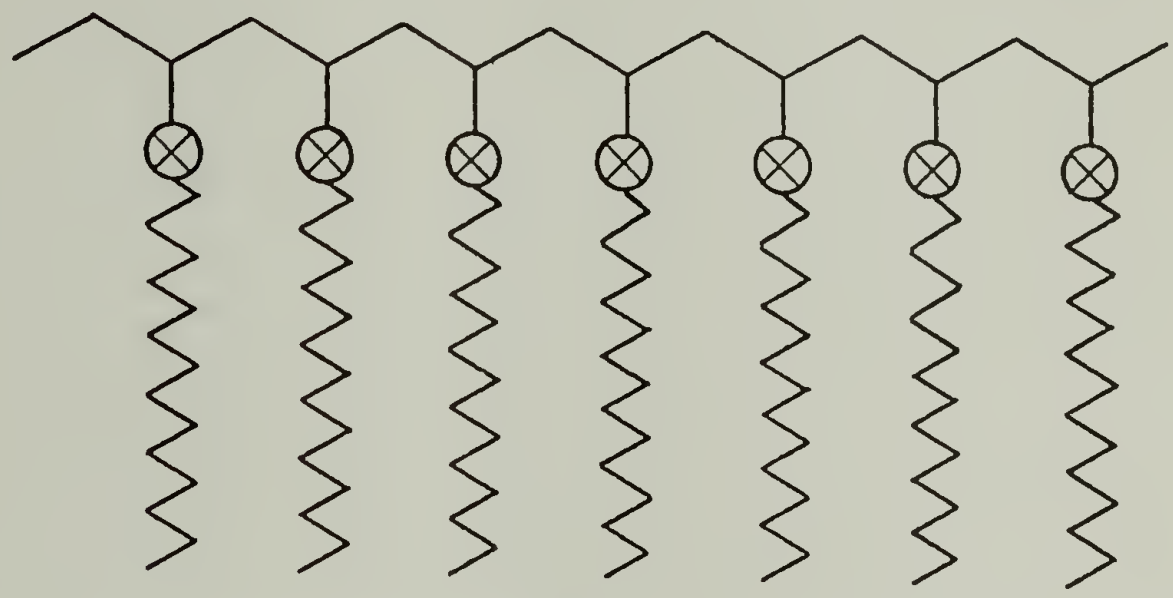
The polymerization of a number of dialdehydes such as glyoxal[93], succinaldehyde[94, 95] and glutaraldehyde[96, 97] has been reported. The structure of the polymer of glyoxal is ill defined. Succinaldehyde and glutaraldehyde give polymers with α-oxyfuran or α-oxypyran repeat units in the polymer backbone. Similarly, phthalaldehyde and malealdehyde have been polymerized to give polymers with cyclic repeat units[98, 99, 100].

D. Comb-like Polymers and Side Chain Crystallization

Polymers having the general structure suggested in Figure 2 can be considered to be members of a class of polymers which is intermediary between the linear and branched macromolecules. These long side chain or "comb-like" polymers consist of two structural entities;

the contiguous polymer backbone and a side chain attached to eacy polymer repeat unit. The way in which the two types of units are joined is another consideration which can have some significance.

Figure 2: Schematic Representation of a Comb Like Macromolecule



Such comb like polymers have been known for a number of years[101, 102] and a number of different polymer types have been reported including poly(α-olefins)[103, 104, 105], poly(n-alkylacrylates) and poly(n-alkylmethacrylates)[78, 106-8], poly(vinyl esters)[78, 109], poly(n-alkyl butadienes)[110], poly(n-alkylacrylamides)[78, 111], and poly(N-n-alkyl hexamethylenemalonamides)[112]. In the case of the vinyl type polymers, comb like polymers having differing tacticity of the main chain are reported, however, in most instances the stereoregularity of the backbone chain is unknown.

Plate and Shibaev[113] have given a review, with 345 references, concerning the structure, fusion behavior, molecular mobility, deformation properties, and dilute and concentrated solution properties of comb like macromolecules. In the remainder of this section most of the discussion will be concerned with the structure and fusion of long side

chain polymers.

Perhaps the first type of comb like macromolecules whose solid state structure was investigated in some detail are the poly(α-olefins). Polymers of this class have a polymethylene backbone with a long normal aliphatic side chain on every other carbon atom of the backbone chain. Typically, the polymers were prepared by Ziegler-Natta type initiation which presumedly resulted in highly stereoregular polymers. Frequently, insufficient attention was paid to fractionation of the polymers and possible contamination of the polymer samples with fractions of lower stereoregularity.

Turner-Jones[103, 104] investigated the solid state structure of a series of poly(α-olefins) from poly(1-hexene) (4 side chain carbon atoms) up to poly(1-octadecene) (16 side chain carbon atoms) which were prepared, under unspecified conditions, with the reaction product of $TiCl_4$ with the reaction product of 1 mole quantity of $LiAlH_4$ with 4 mole quantities of the olefin to be polymerized as the catalyst[114]. The polymers with 4-6 side chain carbon atoms were found to be difficultly crystallizable, stretching of the polymers at low temperatures ($T= -10^oC$ or below) for up to 1 week was normally required to induce crystallization in samples of such polymers. The crystalline polymers with 12 or more side chain carbon atoms were found to be capable of existing in two forms which Turner-Jones designated Type I and Type II. Only one form could be defined for the polymers of intermediate side chain length, such as poly(1-dodecene), and this form was believed to be essentially the same as Type I of the longer side chain polymers.

Type I, typified by quenched samples, was characterized by

spacings of 4.2Å and 4.7Å. Furthermore, the long spacings of Type I varied linearly with the length of the alkyl group and gave slightly diffuse reflections. Type II, typified by slow cooled samples, was characterized by strong reflections corresponding to spacings of 3.57Å and 4.22Å. The reflections of long period spacings of Type II were sharper than for Type I and, for a fixed number of side chain atoms, the Type II long spacings were smaller. Turner-Jones suggested that in Type I the side chains are less efficiently packed and are disposed at right angles to the backbone chain which is likely in a helical conformation. Type II was suggested to involve more efficient side chain packing. An orthorhombic unit cell, in which the side chains are slanted with respect to the axis of the main chain helix, was assumed for Type II.

More recently, the melting transitions of a series of presumed isotactic poly(α-olefins) was investigated by DSC and DTA and many of the general observations of Turner-Jones were confirmed[115]. Two endothermic transitions (T_1; T_3) and one exothermic transition (T_2) ($T_1 \angle T_2 \angle T_3$) could be observed by DSC and DTA in melt quenched samples of poly(α-olefins) having 12-20 side chain carbon atoms. At temperatures below T_1 the x-ray diagrams of all samples were characterized by relatively broad diffraction maxima, the most intense of which corresponded to a spacing of 4.2Å. If the samples were well annealed at a temperature T* ($T_2 \angle T^* \angle T_3$) a greater number of much sharper diffraction maxima could be observed. The authors suggested that the crystallinity in quenched samples at temperatures below T_1 was primarily due to exclusive crystallization of the outer methylene groups

of the side chains. It was suggested that the side chain crystallites melt in the region of T_1 and, with further heating, a new crystal structure develops (exotherm at T_2) which involves both main chains and side chains in an orthorhombic lattice. The new crystal structure then melts at temperature T_3. Depending upon the thermal history and the length of the side chain both types of crystalline structures existed in various relative proportions in samples at temperatures below T_1.

Very similar observations had been made by Aubrey and Barnatt[116] for the case of poly(1-octadecene) prepared with a Ziegler-Natta type initiator. A fraction of the polymer (53%) was soluble in n-hexane at room temperature and could be extracted from the native polymer. The DTA thermogram of a slow cooled sample of the hexane soluble fraction showed only one narrow peak at 41.5°C. A slow cooled sample of the hexane insoluble fraction showed two endothermic peaks, one at 41.5°C (with small low temperature shoulder) which overlapped with a slightly broader endotherm which peaked at 68°C.

The conclusions of Trafara et al[115] were different from those of Turner-Jones, at least in regards to the primary nature of the crystallinity in quenched (Turner-Jones Type I predominates) samples of long side chain poly(α-olefins). Turner-Jones had previously refuted the idea of exclusive side chain crystallinity in poly(α-olefins)[117]. The agreement concerning the nature of the macromolecular packing and crystallinity of slow cooled or well annealed (Turner-Jones Type II predominates) samples of poly(α-olefins) was very close. Some literature data concerning the structure and fusion of comb like poly(α-olefins) is collected Table 1.

TABLE 1

Transition Temperatures and Long Period Spacings of Long-Chain Poly(α-olefins)

Polymer	Transition Temperatures[a] in °C			X-Ray Long Spacing[b] in Å	
	T_1	T_2	T_3	Form I	Form II
Poly(1-dodecene)	-	-	-	29.5	-
Poly(1-tetradecene)	3	14	54	34.5	28.0
Poly(1-pentadecene)	13	20	59	-	-
Poly(1-hexadecene)	28	31	63	39.5	31.6
Poly(1-octadecene)	43 (41)[c]	46	71 (68)[c]	44.5	35.2
Poly(1-docosene)	69	72	92	-	-
Average increase per $-CH_2-$	10[a]		4[a]	2.5	1.8

[a] Data of reference 115

[b] Data of reference 114

[c] Data of reference 116

Comb like poly(n-alkyl acrylates), poly(n-alkyl methacrylates) and poly(vinyl esters) are also known, as are comb like poly(n-alkyl vinyl ethers), and a considerable effort has been concentrated on such polymers. These polymers were prepared by polymerization of the corresponding vinyl monomers. The structure and properties of these polymers were the primary focus of a previously mentioned extensive review article[114]. The experimental evidence available overwhelmingly supports the generally accepted conclusion that crystallinity in the comb like acrylate, methacrylate, vinyl ester, and vinyl ether polymers arises solely from crystallization of the outer paraffinic methylene groups without a definable participation of the backbone chains. In some cases[107] a deliberate attempt has been made to prepare and investigate stereoregular, isotactic long side chain acrylate polymers. However, even in those cases where a significant but undefined stereoregularity was achieved, the crystallization of the polymers still exclusively involved the side chains.

The x-ray diffraction diagrams of all the comb like polymers of these types were extremely similar and showed characteristic reflections corresponding to spacings of 2.1$\mathring{A}$, 2.4$\mathring{A}$, and 4.2$\mathring{A}$. The mode of packing, common to all these polymers, is one in which the side chains are hexagonally packed in a manner which is very similar to the mode of packing which has been observed for n-paraffins[118] and low molecular weight compounds with long n-aliphatic chains. Normally, two long period reflections were recorded for the crystalline polymers (d_1, d_2; $d_1 \perp d_2$; after Plate[114]). The values of the spacings increased in a linear way as the length of the side chain increased. For the comb like

acrylate, vinyl ester, and vinyl ether polymers the intensity of the reflection corresponding to d_1 was much stronger than that corresponding to d_2; this order of intensities was reversed for the comb like poly(n-alkyl methacrylates).

By comparison with low molecular weight compounds having long n-aliphatic groups and because the spacings calculated assuming an extended conformation of the side chain agreed very well with the observed values it has been concluded that two types of arrangements of the hexagonally packed side chains may occur. A two layer type of arrangement is believed to predominate in the acrylate, vinyl ester, and vinyl ether polymers, whereas a one layer type of arrangement is believed to predominate in the case of the methacrylate polymers. However, both types of arrangements were thought to coexist in all the comb like polymers being discussed here. The volume and conformational requirements of the stiffer methacrylate backbone chain impose greater restrictions on conformational changes of the side chain at the attachment bridge, thus hindering the attainment of an extended conformation in the side chains and thereby influencing their packing. Other situations such as quenching, which also would be expected to adversely affect packing, similarly promoted the one layer type of packing.

Jordan[78] has investigated the fusion behavior of polymers of long chain acrylates, acrylamides, and vinyl esters and found that the observed heats of fusion of the polymers could be fitted by an equation of the form of Equation 6;

$$\Delta H_f \text{ (cal/mole)} = \Delta H_f^e + a(n) \qquad \text{Eqn. 6}$$

where ΔH_f^e is a constant, reflecting contributions of chain (or side chain) ends; a is the slope of the line, in cal. $mole^{-1}$- CH_2, and represents the increment in the heat of fusion per methylene unit; and n is the number of methylene units in the side chain of each repeat unit, counting the terminal methyl group.

The similarity in the way the several measured and derived thermodynamic variables depend upon n between the long side chain polymers and the n paraffins of similar number of methylene groups and the similarity between the hexagonal packing of the side chains and the analogous structuration of n-paraffins just below their melting point suggested that the thermodynamic data for the α_H-l transition of the n-paraffins[118] might suitably fit the melting transitions of the side chains. Indeed, Jordan[78] has estimated the crystallinity of the side chains and the average number of methylene groups per side chain participating in crystallization for several types of comb like polymers by assuming a model for the side chain crystallization based upon the α_H-l transition of n-paraffins. The calculated value of the average number of crystallizing methylene groups per side chain compared reasonably well with the number indicated by the value of n at $\Delta H=0$, Equation 6.

The effect of certain solvents on the heat of fusion of the long side chain polymers was taken as further evidence that only the outer paraffinic methylene groups participate in the crystallization of the polymers and served to further illustrate the more subtle role of the side chain attachment bridges in influencing side chain crystallization. The heats of fusion and shapes of the DSC thermograms were very

similar for the poly(n-alkyl acrylates) and poly(vinyl esters) of essentially the same side chain length. However, the heats of fusion were lower and the fusion endotherms broader for the poly(n-alkyl acrylamides) as compared to their acrylate and vinyl ester counterparts. If the long side chain polyacrylamides were treated with methanol, a non-solvent for the polymers, the fusion endotherms became more narrow, the peak temperature increased slightly, and the heats of fusion of the polyacrylamides much more closely resembled the heat of fusion of the acrylate or vinyl ester polymers of similar side chain length. The methanol was believed to act by selectively solvating the polar groups attached to the backbone chain thereby allowing more methylene groups to enter into hexagonally packed crystallites of more narrow size distribution.

The heats of fusion of copolymers of n-alkyl acrylates whose homopolymers exhibit side chain crystallization vary with composition in a nearly linear way over the entire composition range. The heats of fusion of copolymers of long chain acrylates with short chain acrylates (e.g. ethyl acrylate) decrease regularly with increasing content of short chain comonomer, following a pattern which corresponds to a simple dilution of the crystalline component[119].

For the comb like acrylate, methacrylate, vinyl ester, vinyl ether, and acrylamide polymers a side chain length of 10-12 carbon atoms was required in order to observe the phenomenon of side chain crystallization. In the case of poly(α-olefins), prepared with Ziegler-Natta type initiators, it was very difficult to detect crystallinity in polymers having 4 to 7 carbon atoms in the side chain, whereas crystalline

poly(α-olefins) with 12 or more side chain carbon atoms were known to exist in two forms. In one of these forms the crystallization of the polymer may well be controlled by the polymer side chains.

Higher aliphatic aldehyde polymers, which were shown to be highly isotactic when these were prepared with certain soluble anionic initiators, exhibited transitions which were best attributed to "melting" of the paraffinic side chains at side chain lengths as short as 4 carbon atoms[15, 76]. Comb like polyaldehydes are perhaps more similar to the poly(α-olefins) than the other types of comb like polymers in that there is no attachment bridge or spacer group between the backbone and the side chain. However the poly(α-olefins) and the polyaldehydes are notably different in that the polarities of the main and side chains are different in the case of the isotactic polyaldehydes. Furthermore, for the lower members of the respective homologous series, the melting point of the polyaldehyde is always greater than the melting point of the corresponding polyolefin.

In the case of crystalline polyheptanal two transition regions have been established. The transitions of the first transition region ($70^{o}C$ to $100^{o}C$) have been associated with the melting of the side chains which are packed in a loose hexagonal array[22]. Data for the first transitions of a number of polyaldehydes (up to n-octaldehyde) gave values for a number of thermodynamic quantities which resembled the values for the α_H-1 transition of n-paraffins. Evidence from x-ray investigations[68] strongly suggested that polyheptanal may exist in a crystalline form in which both the main chains and side chains participate in the crystal lattice. The observation of two transition

regions for higher aliphatic polyaldehydes and the subtle difference in crystal structure between polyheptanal and, for example, polypropanal indicate an increasing influence of the aliphatic side chain on the polymer crystallization.

The question may then be posed; if polyaldehydes having still longer side chains could be prepared, might some side chain length be reached where the crystallization of the polyaldehydes would be controlled by the packing requirements of the paraffinic side chains? The synthesis and characterization of polyaldehydes having side chain lengths greater than those previously reported forms the subject of this thesis.

I I

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ients

Infrared spectra were ith either a Perkin-Elmer Model 727
or Model 283 spectrophotomet- n-Elmer Corporation, Norwalk,
Conn.). Liquid compounds wer ed neat between NaCl plates or in
solution (3-6%, in $CHCl_3$ or C olid compounds were examined as
KBr pellets or in solution (3- $CHCl_3$ or CCl_4). Polyaldehyde
samples were frequently exami ne form of thin films cast directly
from a $CHCl_3$ solution or high en "gel" of the polymer onto a
NaCl plate.

PMR spectra were recorded ither a Perkin-Elmer Model R-24,
60MHz, or Model R-32, 90MHz, eter (Perkin-Elmer Corporation,
Norwalk, Conn.). The latter i nt was equipped with both the
field-frequency lock and doubl ance accessories. All samples were
measured as solutions of 5-20 tration in $CDCl_3$. Chemical shifts
were measured as δ, ppm. relat TMS as internal standard.

CMR spectra were recorded Bruker model fourier transform
spectrometer. Samples were me as solutions of 15-20% concentra-
tion in $CHCl_3$, which also serv he internal standard.

Gas chromatographic analy) were conducted with a Varian
Model 1400 gas chromatograph (Associates, Palo Alto, Calif.)
equipped with a thermal conduc detector. For the analysis of
aldehyde monomers a 6' x 1/8" .318cm.) Carbowax 20M (5% on
100/120 Chromasorb W, AW, DMCS n was employed. The column oven

was operated in the temperature programmed rather than the isothermal mode. The initial and final column oven temperatures and the heating rate were varied according to the aldehyde being analyzed. All other gas chromatographic analyses were conducted isothermally employing a 3' x 1/8" (91.4 x 0.318cm.) Porapak Q column. Helium (60 psig. inlet pressure) was used as the carrier gas at a flow rate of 30ml./min..

Thermogravimetric analyses were performed with a Perkin-Elmer Model TGS-1 thermobalance with UU-1 temperature programmer (Perkin-Elmer Corporation, Norwalk, Conn.). The temperature scale of the programmer was calibrated with the magnetic standards provided with the instrument in order to optimize the agreement between the direct dial readout of the temperature programmer and the instrument furnace temperature, as indicated by transitions of the standards. The agreement over the temperature range of interest could conveniently be brought to within $5^{o}C$. Heating rates of $10^{o}C$/min. or $20^{o}C$/min. were normally employed and all thermogravimetric measurements were performed under a 10-20 cc./min. flow of dry N_2. Samples (2-7mg.) were weighed to the nearest 0.002mg. into aluminum or platinum sample pans on a Mettler Micro Gram-Atic analytical balance (Mettler Instrument Corporation, Hightstown, N.J.).

Thermal transitions in samples were investigated employing either a Perkin-Elmer Model DSC-1B or Model DSC-2 differential scanning calorimeter (Perkin-Elmer Corporation, Norwalk, Conn.). The temperature scale of the instrument was calibrated at the desired heating rate by adjusting the direct dial average temperature readout of the programmer to correspond with the transition temperature of cyclohexane (m.p.=$+6^{o}C$) and indium (m.p.=$156^{o}C$). The suitability of the temperature calibration

was judged by noting the observed transition temperature of either p-nitrotoluene (m.p.=51.5^{o}C) or napthalene (m.p.=80.2^{o}C), or both. The calibration was judged adequate if these transitions were observed within 3^{o}C of their reported values.

Samples were contained in sealed, volatile style sample pans fabricated of aluminum. Similar sample pans, fabricated of gold, were employed for the DSC investigation of aldehyde monomers. Prior to their use, all sample pans were washed with $CHCl_3$ and dried. Powder, clump, or filament samples were placed into tare weighed sample pan assemblies, the pans were sealed and then reweighed to determine the sample weight. All weighings were made to the nearest 0.002mg. on a Mettler Micro Gram-Atic analytical balance (Mettler Instrument Corporation, Hightstown, N.J.).

The sample size, heating rate, ordinate sensitivity (mcal s^{-1} for full scale recorder pen deflection), and recorder chart speed were varied according to the requirement and scope of the individual measurement. A heating rate of 20^{o}C/min. was most commonly employed and the recorder chart speed was usually adjusted so that the numerical value of the chart speed (in mm./min.) equaled twice the numerical value of the heating rate (in deg.C/min.). All measurements were made under a 20-30cc./min. flow of dry N_2.

Peak areas were measured with plainimeter and transition enthalpies were calculated by comparing the area under the sample peak against the area under the fusion peak of a known weight of cyclohexane (7.47cal./g.), or indium (6.79cal./g.).

In some cases changes in a sample as a function of temperature

and/or thermal transitions of a sample were visually observed employing a polarizing light microscope equipped with a Mettler FP2 heating stage accessory (Mettler Instrument Corporation, Hightstown, N.J.) at a programmed heating rate of 10^{o}C/min. or 2^{o}C/min.. The temperature calibration of the heating stage at a heating rate of 10^{o}C/min. was checked with p-nitrotoluene (m.p.=51.5^{o}C) and benzoic acid (m.p.=122.3^{o}C) both of which melted within 0.5^{o}C of the reported temperature.

A Mel-Temp capillary melting point apparatus (Laboratory Devices, Cambridge, Mass.) was also employed for the visual determination of the melting points of some samples. Temperatures reported from such measurements are uncorrected.

X-ray diffraction diagrams were obtained with a Phillips diffractometer (North American Phillips Company, Mt. Vernon, N.Y.) employing the flat film transmission technique and were recorded on Kodak no-screen medical grade x-ray film (Eastman Kodak Company, Rochester, N.Y.). Nickel filtered CuK radiation (35kV.; 20ma.) was employed with pin-hole columniation. Powder samples were examined as ca. 1mm. plugs of lightly packed powder. Filament samples were examined as single filaments.

Vapor pressure osmometry (VPO) determinations of number average molecular weight were normally performed in $CHCl_3$ at 37^{o}C by the Microanalysis Laboratory, Office of Research Services, University of Massachusetts. VPO measurements conducted by the author were performed at 37^{o}C in benzene using an HP-302 vapor pressure osmometer (Hewlett Packard Company, Palo Alto, Calif.), benzil was used as the standard.

Elemental analyses were performed by the Microanalysis Laboratory,

Office of Research Services, University of Massachusetts.

B. Chemicals

The following chemicals were obtained from the indicated sources.

1. Reagents.

Acetic Anhydride (E)

Acetyl Chloride (E)

Apiezon N (J.G.B.)

Antimony Pentachloride (MCB)

Benzil (E)

Benzoic Acid (TherMetric) (F)

Chloral (M)

Calcium Chloride-Anhydr. (F)

Calcium Hydride (F)

Cyclohexane (99 mole %) (F)

Decanal (A)

Dimethylacetamide (A)

2,4-Dinitrophenylhydrazine

N,N'-Di-β-napthyl-p-phenylene-diamine (E)

Dodecanal (A)

Drierite (Granular $CaSO_4$, anhyd.) (WH)

Hexanal (A)

Hydrochloric Acid (N/1) (F)

Lithium-t-Butoxide (AV)

p-Nitrotoluene (TherMetric) (F)

Nonanal (A)

Phosphorous Pentoxide, Granular (JTB)

Potassium Bromide, spectrophotometric (H)

Potassium Hydroxide, Flake (F)

Pyridine (E)

Soda Lime (F)

Sodium, Metallic (F)

Sodium Bicarbonate (F)

Sodium Bisulfite (F)

Sodium Carbonate, Anhyd. (F)

Sodium Carbonate, Monohydrate (F)

Sodium Hydroxide, Electrolytic pellets (F)

Sulfuric Acid (F)

Tetramethylsilane (A)

Triethylorthoformate (E)

Magnesium Sulfate, Anhyd. (F)

Methyl Orange (E)

Molecular Sieves-3A (MCB)

Napthalene (TherMetric) (F)

Undecanal (A)

2. Solvents.

Acetic Acid, Glacial (F)

Acetone, Spectrograde (F)

Benzene, Spectrograde (F)

2-Butanol (E)

Carbontetrachloride (M)

Deuterochloroform, 1% TMS (A)

Dichloromethane (F)

Diethyl Ether (F)

Diethyl Ketone (E)

Dimethylformamide (A)

Ethanol, 95% (F)

Glycerin (F)

n-Hexane (F)

Methanol (F)

Methylcyclohexane (E)

i-Octane (E)

n-Pentane (F)

2-Propanol (F)

Tetrahydronapthalene (E)

Toluene, Spectrograde (F)

3. Sources.

A	Aldrich Chemical Company, Milwaukee, Wisc.
AV	Alfa Products, Danvers, Mass.
E	Eastman Organic Chemicals, Rochester, N.Y.
F	Fischer Scientific Company, Pittsburg, Penn.
H	Harshaw Chemicals, Solon, Ohio
JTB	J. T. Baker Company, Phillipsburg, N.J.
J.G.B.	J. G. Biddle Company, Plymouth Meeting, Penn.
MCB	Matheson Coleman & Bell, Norwood, Ohio
M	Montrose, Chemical Division, Boston, Mass.
WH	W. H. Hammond, Xenia, Ohio

C. Purification of Reagents and Solvents

1. Aliphatic aldehyde monomers. Depending upon the nature and scope of the experiment in which the aliphatic aldehyde was to be used, one of the three following purification schemes was employed. Except where noted, all glassware, syringes, and syringe needles used in the purification scheme, or used in subsequent handling of the aldehyde, were soaked for several hours in warm (ca. 60°C) 2% Micro cleaning solution (International Products Corporation, Trenton, N.J.), rinsed well with distilled water, and dried for at least 3 hrs. in an oven maintained at 110°C. The glassware was assembled hot and cooled under a blanket or stream of dry N_2 or, alternatively, in a dessicator over granular P_2O_5. When aliphatic aldehydes were distilled a small amount (0.1%) of N,N'-di-β-napthyl-p-phenylenediamine was routinely added to the still pot. In all reduced pressure distillations of aliphatic aldehydes a magnetic stirrer was used to maintain vigorous

agitation of the contents of the still pot, a manostat was normally used to stabilize the pressure. Apiezon grease was exclusively used for the lubrication of ground-glass surfaces.

Procedure I: The aldehyde, taken from a freshly opened stock bottle, was stirred with sodium carbonate monohydrate (ca. 0.05g./ml. of aldehyde) at room temperature for 3-5 hrs. under a blanket of dry N_2. The stirrer was stopped and the suspension was pressure filtered (N_2 pressure) with dispatch through a coarse fritted funnel directly into an open flask. A syringe needle connected to a source of dry N_2 and extending through the open neck of the collection flask was used to maintain an atmosphere of N_2 over the filtrate as it was collected. The capacity of the funnel was chosen so that the entire volume of the suspension could be accommodated at one time.

When the filtration was complete a magnetic stirring bar and a small amount of CaH_2 (ca. 0.02g./ml. of aldehyde) was placed into the flask containing the aldehyde. The flask was then closed with a rectangular adapter with stopcock which was connected, via a glass tee, to a N_2 source and a mineral oil bubbler. The flask was clamped in place in an ice bath and the contents of the flask were magnetically stirred for 1-3 hrs. at $0^{o}C$. The stirring was discontinued, the ice bath removed, and the flask and its contents were allowed to warm to room temperature. The aldehyde was separated from the resulting tight slurry by pressure filtration exactly as described above. The vessel containing the filtered aldehyde was closed with a mating ground glass joint fitted to a 3-way stopcock in such a way that, with proper manipulation of the cock, a syringe needle could be inserted through the

stopcock directly into the vessel, giving access to the contents of the vessel, while maintaining a stream of N_2 through the third arm of the 3-way stopcock. Approximately 85% of the original volume of crude aldehyde was obtained. In some cases molecular sieves (3A) were added to the aldehyde before the vessel was closed. The aldehyde was used within 48 hrs..

Procedure II: In this procedure the aldehyde was treated exactly as in procedure I excepting that, after the aldehyde was stirred with CaH_2 at 0^oC, the stopcock of the rectangular adapter was closed, the assembly disconnected from the N_2 line and removed from the ice bath, and stored in the freezer (-15^oC) overnight.

The vessel was removed from the freezer and the vessel and its contents were allowed to warm to room temperature. A significant amount of dark grey solid material, presumedly CaH_2 and $Ca(OH)_2$, remained suspended in the now slightly yellow aldehyde. The suspension was pressure filtered through a medium fritted funnel directly into an open round-bottomed microglass flask. A syringe needle connected to a source of dry N_2 and extending through the open neck of the flask was used to maintain an atmosphere of N_2 over the filtrate as it was collected. When the filtration was complete a small amount of CaH_2 ($<$0.005g./ml. of aldehyde) was added to the flask containing the filtrate and the flask was mounted on a distillation apparatus. The distillation apparatus was connected to a vacuum pump and the aldehyde was distilled at reduced pressure through an 18cm. microglass Vigreux column which was wrapped well with fiberglass insulation. A multiple fraction cutter was employed. Normally, a fore cut amounting to 10-15% of the

pot charge and a main cut amounting to 40-60% of the pot charge were collected.

In order to minimize possible side reactions of the aldehydes in the still pot and, perhaps, on the glass surfaces of the distillation apparatus, heating of the contents of the still pot was kept to a minimum commensurate with a minimum practical distillation rate. Thus, particularly in the case of the higher boiling aldehyde dodecanal, the loading of the distillation column may have been insufficient to maintain the bulb of the thermometer, at the top of the column, in equilibrium with vapor. This condition might explain the fluctuating boiling points which were recorded in some distillations of the higher aldehydes. Also, at pressures below ca. 0.6mm. Hg, the manostat was less effective in stabilizing the pressure. Representative data obtained during the distillation of the respective higher aliphatic aldehydes is collected in table 2, together with the column oven conditions used in GC analysis of the aldehydes.

At the termination of the distillation N_2 was admitted into the still (Hg filled check valve). The flask containing the main fraction was removed from the fraction cutter under a positive pressure of N_2 and rapidly closed with a serum stopper. In some cases the main cut was transferred, via syringe and under N_2, to a ground-glass jointed vessel containing molecular sieves (3A) closed with a mating ground-glass joint fitted with a 3-way stopcock as previously described. The aldehyde was stored in this manner prior to its use for up to 48 hrs. at room temperature in the dark. Storage of the higher aliphatic aldehydes in contact with molecular sieves for a longer period of time

TABLE 2

Reduced Pressure Boiling Points of Higher Aliphatic Aldehydes and GC Column Conditions

ALDEHYDE	B.P. (in ^{o}C)	PRESSURE (in mm. Hg)	GC COLUMN OVEN CONDITIONS T_{C_i}	T_{C_f}	Rate
Hexanal	60	65	---	---	----
Nonanal	68 - 69	7.4	100^{o}	150^{o}	12^{o}/min.
	62 - 63	5.0			
	40 - 45	1.0			
Decanal	44 - 46	0.6	130^{o}	170^{o}	12^{o}/min.
	36 - 40	0.2			
Undecanal	53 - 55	0.6	145^{o}	195^{o}	15^{o}/min.
	49 - 51	0.2			
Dodecanal	67	0.5	160^{o}	205^{o}	15^{o}/min.

(>1wk.) was found to cause marked visible deterioration of the aldehyde.

Procedure III: For the more critical polymerization experiments the main fraction, obtained exactly as outlined above in procedure II, was immediately redistilled at reduced pressure from the flask in which it was collected through a one-piece 10cm. microglass Vigreux column fitted with a Claisen distilling head which was wrapped well with fiber-glass insulation. A multiple fraction cutter was employed. Normally a fore cut amounting to 5-10% of the pot charge and a main cut amounting to 40-50% of the pot charge was collected. At the termination of the distillation N_2 was admitted to the still (Hg filled check valve) and the flask containing the main cut was removed from the fraction cutter under a positive pressure of N_2 and quickly closed with a serum stopper. The aldehyde was used immediately after distillation.

The water content of the thus purified aldehydes was estimated to be less than 0.04% by GC. The gas chromatograms of nonanal and decanal exhibited a small pronounced peak on the generally broad tail on the high retention time side of the major aldehyde peak. This peak was assumed to be due to the presence of the corresponding fatty acid in the aldehydes according to the rancid odor of the column effluent.

Similarly, the water content of the nonanal and decanal was believed to be on the order of 0.05%. Although a rancid odor was noted in the effluent volume past the main aldehyde peak in the gas chromatographic analysis of undecanal and dodecanal, the resolution achieved was not sufficient to allow a more precise estimation of the acid contents of these aldehydes to be made.

2. Other Reagents and Standards. Acetic anhydride was refined by treating it with 30% of its volume of dry toluene, the resulting mixture was then fractionally distilled through a 35cm. vacuum jacketed Vigreux column under a blanket of dry N_2. Several small pieces of silicon carbide were used to suppress bumping. The still pot was heated at reflux until the head temperature reached 103°C. The acetic acid-toluene binary azeotrope was collected at a reflux ratio of ca. 1:1 (b.p.=103-106°C; lit.[120] b.p.=105.4°C). Collection was continued as the head temperature rose to 111°C, the receiver was changed and toluene was collected at a reflux ratio of 1:1 (b.p.=111-112°C). When the head temperature rose to 130°C the reflux ratio was increased to 5:1, and a fraction (ca. 5% of the initial volume of anhydride) was collected (130-134°C) and discarded. The receiver was changed and acetic anhydride (b.p.=134°C) was collected at a reflux ratio of 5:1. Approximately 75% of the original volume of the anhydride was collected.

Antimony pentachloride was distilled at reduced pressure (b.p.=82-85°C at 25mm. Hg). A N_2 ebulator was used to suppress bumping.

Commercially obtained chloral was purified according to procedures established in our laboratory. Chloral of sufficient purity could be stored for up to 10 hrs. under N_2 in the dark before use.

Cyclohexane, used as a standard in differential scanning calorimetry, was magnetically stirred with CaH_2 (0.1g./ml. cyclohexane) then twice distilled from CaH_2 under a blanket of dry N_2 through a one-piece 10cm. microglass Vigreux column with Claisen distilling head (b.p.=80.5-81°C). The contents of the still pot were magnetically stirred during the distillation. In each distillation a heart cut

amounting to 60% of the pot charge was collected.

Lithium-tertiary-butoxide (LTB) was sublimed at 120°-150°C and reduced pressure (0.1mm. Hg). LTB initiator was used as its methyl-cyclohexane (MCH) solution. All manipulations of the sublimed alkoxide were conducted in a N_2 filled glove bag. (Instruments for Industry and Research, Cheltenham, Penn.).

Molecular sieves (3A) were activated by heating them to 250-290°C at reduced pressure (0.01mm. Hg) for 12 hrs..

Sodium carbonate, used for the standardization of aqueous mineral acid solutions, was dried in an oven at 120°C for 8 hrs..

3. Solvents. Diethyl ether was dried in a tightly capped bottle over molecular sieves (3A).

n-Hexane was magnetically stirred with CaH_2 (0.1g./ml. n-hexane) overnight. The n-hexane was then distilled through a 30cm. Vigreux column at a reflux ratio of 5:1 under a blanket of dry N_2 (b.p.=69°C). The contents of the still pot were magnetically stirred during the distillation. A heart cut amounting to 70-80% of the pot charge was collected and transferred to a drying column filled with molecular sieves. The top reservoir of the column was closed with a rectangular adapter with stopcock which could be attached to a source of dry N_2. The bottom of the column was fitted with a 3-way stopcock, one arm of which was terminated with a Luer-lok fitting so that, if desired, the solvent could be withdrawn directly with a syringe.

MCH (600ml.) was refluxed with sodium (30g.) and crude LTB (4g.) for 14 hrs.. The MCH was then filtered, refluxed with fresh sodium under a blanket of dry N_2 for 3-4 hrs. on the distillation apparatus to

be used, and distilled from sodium under a blanket of dry N_2 through a 30cm. Vigreux column at a reflux ratio of 2:1 (b.p.=101^{o}C). A heart cut amounting to 85% of the pot charge was collected directly into a clean, dry reagent bottle. At the termination of the distillation the receiver bottle was removed from the still and sodium wire was pressed into the bottle. The bottle was closed with a ground glass stopper and the bottle and its contents were allowed to stand at room temperature for 24 hrs.. During this period the surface of the sodium wire deteriorated only slightly.

The MCH was then decanted into a clean, dry reagent bottle and fresh sodium wire was pressed into the bottle containing the MCH. The bottle was then closed with a mating ground glass joint fitted with a 3-way stopcock, in the same manner as previously described. After 48 hrs. the appearance of the surface of the sodium wire in the MCH was essentially unchanged and the solvent was ready for use.

n-Pentane was dried in a tightly closed bottle over molecular sieves (3A).

Toluene (600ml.) was refluxed with sodium (30g.) and crude LTB (3g.) for 14 hrs.. Toluene was then filtered and refluxed overnight with fresh sodium under a blanket of dry N_2 on the distillation apparatus to be used. Toluene was then distilled from the sodium under a blanket of dry N_2 through a 30cm. Vigreux column at a reflux ratio of approximately 10:1 (b.p.=111^{o}C). A heart cut amounting to 85% of the pot charge was collected directly into a clean, dry reagent bottle. At the termination of the distillation the receiver bottle was removed from the still and sodium wire was pressed into the bottle. The bottle

was closed with a ground glass stopper and the bottle and its contents was allowed to stand at room temperature for 24-48 hrs.. During this period there was a moderate deterioration of the surface of the sodium wire in the toluene.

Toluene was decanted into a clean, dry solvent bottle and fresh sodium wire was pressed into the bottle containing the toluene, the bottle was closed with a ground glass stopper, and the bottle and its contents were allowed to stand at room temperature for 24 hrs.. The liquid was again decanted and sodium wire was pressed into the liquid, this time the bottle was closed with a mating ground glass joint fitted with a 3-way stopcock, in the same manner as previously described. After 24-48 hrs. the appearance of the surface of the sodium wire in the toluene was essentially unchanged and the solvent was ready for use.

D. Special Procedures and Equipment

1. Procedures. All transfers and manipulations of monomers, solvents, and initiators for the aliphatic aldehyde polymerizations were performed under N_2 using a hypodermic syringe. All syringes and needles were soaked for several hours in warm (ca. $60^{o}C$) 2% Micro cleaning solution, rinsed well with distilled water, and dried for at least 14 hrs. in an oven maintained at $110^{o}C$. The syringe assemblies were either used directly from the oven or were allowed to cool for a time in a dessicator over granular P_2O_5.

All glass or metallic parts of the apparatus used in the polymerization of aliphatic aldehydes were soaked for several hours in warm (ca. $60^{o}C$) 2% Micro cleaning solution, rinsed well with distilled

water, and dried for at least 14 hrs. in an oven maintained at 110°C. The polymerization apparatus was assembled hot and cooled in place filled with a blanket of dry N_2. When test tubes were used as the polymerization vessel these were cleaned and dried as above and cooled in a dessicator over granular P_2O_5 prior to their use. Apiezon N grease was exclusively used for the lubrication of all ground glass joints.

For the more critical polymerization experiments, particularly those experiments in which the temperature history of the polymerization reaction was closely controlled, a slightly different procedure was used to prepare the polymerization apparatus. All components were soaked for several hours in warm (ca. 60°C) 2% Micro cleaning solution, rinsed well with distilled water, and dried for at least 14 hrs. in an oven maintained at 135-140°C and assembled hot.

A three-necked round-bottomed flask (250ml. or 500ml.) was fitted with two ground-glass stoppers and a male ground-glass joint fitted to a 3-way stopcock in a manner as previously described. The stopcock was attached to a vacuum pump and the apparatus was evacuated to 0.01mm. Hg, heated for ca. 15 min. with the flame of a Fisher burner, and allowed to cool to room temperature while evacuated. The flask was filled with dry N_2 and returned to the 135-140°C oven for ca. 1 hr.. The stoppers were removed and the flask was fitted with a paddle type stirrer with glass bushing and a Teflon thermometer adapter fitted with a short piece of glass rod. The polymerization apparatus was clamped in place and allowed to cool to room temperature under a blanket of dry N_2. The assembled polymerization vessel was then ready to receive

the ingredients of the polymerization reaction.

Prepurified nitrogen (99.995% min., Airco, Riverton, N.J.) was used in all procedures requiring N_2. Copper, glass, or butyl rubber tubing was used as a conduit for the N_2. When used to blanket aldehyde polymerization reactions the N_2 was first passed through a 20 x 2.6cm. column filled with granular P_2O_5.

For the DSC investigation of the aliphatic aldehyde monomers the monomers were handled and sealed in the gold sample pans in a glove bag filled with Argon (grade 5, 99.9995% min., Airco, Riverton, N.J.).

2. Equipment. In certain polymerization reactions it was desired to exercise more flexible control of the temperature of the bath in which the polymerization vessel was immersed. For this purpose the low temperature bath described below was constructed.

A Dewar vessel (ca. 1900ml. capacity) was fitted with a coil, fashioned from 1/4" o.d. copper tubing, which fit snugly against its wall. One end of the coil was brazed to a short length of 1/4" o.d. copper tubing with a 90^{o} bend which extended to the bottom of a well insulated liquid nitrogen container. The other end of the coil was connected, via a length of rubber vacuum tubing, to the inlet side of a normally closed solenoid valve (Valcor Engineering Company, Kenilworth, N.J., model 94C19C6). The outlet side of the solenoid valve was connected via rubber vacuum tubing to a rough vacuum (20-40mm. Hg). Power to the solenoid valve was controlled by a relay device which was activated by a signal from the bridge circuit in the temperature controller (Yellow Springs Instrument Company, Yellow Springs, Ohio, model 63RC). A probe (#633) immersed in the magnetically stirred bath

medium formed one leg of the bridge circuit. The bath temperature could be easily controlled to $\pm 1^{o}C$.

E. Cyclic Trimers of Higher Normal Aliphatic Aldehydes

1. 2,4,6-Tri-n-octyl-1,3,5-trioxane (nonanal cyclic trimer).

a. Preparation in diethyl ether-pentane with $SbCl_5$ catalyst.

A clean, dry 50ml. round-bottomed microglass flask containing a magnetic stirring bar was fitted with a rectangular adapter with stopcock which was attached to a source of dry N_2. The adapter was momentarily raised and the flask was charged with n-pentane (15ml.) and diethyl ether (15ml.) under a stream of dry N_2. The flask was immersed in an ice bath and the magnetic stirrer was started. After a period of 30 min. the adapter was momentarily raised and $SbCl_5$ (0.5ml., 0.004 mole) was pipetted into the flask under a stream of N_2. The contents of the flask became cloudy. Similarly the flask was then charged with nonanal (5ml., 0.03 mole) and the reaction mixture developed a yellow-brown color. The reaction mixture was magnetically stirred for a period of 25 min. while the bath was maintained at $0^{o}C$. The bath and the reaction flask and its contents were then allowed to gradually warm to room temperature in 1.5 hrs.. After an additional period of 2 hrs. 8 drops of 10% aq NaOH was added to the reaction mixture and most of the yellow-brown color of the reaction mixture was immediately discharged. The reaction mixture appeared as a two phase system. The dense milky white lower phase, approximately equal in volume to the volume of NaOH solution added, was not well dispersed by the magnetic stirrer. After

a period of 10 min. the stirrer was stopped, the rectangular adapter with stopcock was removed, and the narrow end of an eyedropper, connected to a source of compressed air, was inserted through the open neck of the flask. The eyedropper was adjusted so that the tip of the dropper was just above the level of liquid in the flask and a gentle stream of air was directed at the surface of the reaction mixture in the flask. After a period of 1 hr. the volume of the reaction mixture had decreased to 1/3 of its initial volume.

Methanol (20ml.) was added to the flask while the contents of the flask were magnetically stirred. The stirrer was stopped and the flask was stoppered and swirled in an ice bath. A voluminous white precipitate with a milky white supernatant was observed. The stoppered flask was stored overnight in the freezer (-15^{o}C).

The flask was removed from the freezer and the suspension was immediately suction filtered through a cold coarse fritted funnel. The solid was washed with chilled ethanol (2x10ml.), dried on the funnel for 30 min., and dried overnight at room temperature and 20mm. Hg. Yield 0.9g. (22%).

The infrared spectrum (KBr) (pg. 255) showed strong absorptions in the region of 2975 to 2825cm.$^{-1}$ (ν_{as} and ν_{s}; CH_2 and CH_3) as well as at 1465cm.$^{-1}$ (δ_{s}; CH_2). A moderately strong absorption, having several shoulders, was recorded at 1360cm.$^{-1}$ (τCH_2, ωCH_2, δ_{s}; CH_3). A moderately strong slightly broadened peak was recorded at 1150cm.$^{-1}$ which was followed by a sharp peak at 1120cm.$^{-1}$. A doublet was recorded in the region of 720cm.$^{-1}$.

The product was unaffected when a sample was warmed with 20% aq

NaOH in a test tube at 60°C for 15-20 min.

When 50% aq H_2SO_4 was added to a small sample of the product in a test tube the product was immediately transformed into a yellowish oil and the test tube became warm to the touch. The oil gradually thickened and darkened over a period of several hours when the test tube and its contents were allowed to stand at room temperature. The oil was believed to consist of a mixture of aldehyde, aldol condensation products, and oxidation products of the same.

b. Preparation in bulk with H_2SO_4 catalyst.

A 50ml. round-bottomed microglass flask containing a magnetic stirring bar was fitted with a rectangular adapter with stopcock which was connected to a source of dry N_2. The adapter was momentarily raised and the flask was charged with once distilled nonanal (24.8g., 0.17 mole) via syringe and under N_2. The stirrer was started and 2 drops of concentrated H_2SO_4 was added to the aldehyde in the flask. Over a period of 5 min. the reaction mixture became slightly cloudy and discolored and the flask became very warm, and then cooled gradually to room temperature over a period of 40 min.. The reaction mixture was then stirred at room temperature for a period of 1.5 hrs.. The stirrer was stopped and the reaction mixture was added to 65ml. of an ethanol-diethyl ether mixture (1 volume of diethyl ether diluted to 2.5 times its volume with ethanol) in a 125ml. Erlenmyer flask.

The flask was cooled in a CO_2(s)-methanol mixture and the resulting precipitate was recovered from the suspension by suction filtration, washed on the filter with the diethyl ether-ethanol mixture (2x50ml.), dried on the filter for 1 hr., transferred to a crystallizing dish, and

dried in air overnight. Crude yield, 14.2g. (57%).

The crude product (14.2g.) was transferred to a 250ml. Erlenmyer flask and dissolved in $CHCl_3$ (90ml.). The solution was cloudy with no easily distinguishable particulates or liquid droplets. Ethanol (50ml.) was added to the solution in the Erlenmyer flask and the solution became clear. The solution was filtered through a medium fritted funnel into a round bottomed flask and concentrated at room temperature on a rotary evaporator at reduced pressure (20mm. Hg). The milky white residue (ca. 20ml.) was taken up in 75ml. of diethyl ether-ethanol mixture (1 volume of diethyl ether diluted to 2.5 times its volume with ethanol). The mixture was cooled to $-20^{o}C$ (ice-salt bath) which resulted in the formation of a thick suspension which was suction filtered. The solid was washed well with the cold solvent mixture, dried on the filter for 20 min., and dried overnight in air (8.5g., 60% recovery).

The infrared spectrum (KBr) (pg. 255) agreed with that obtained for the nonanal cyclic trimer described in E.1.a. above. The sample softened considerably when ground with KBr in the still slightly warm mortar. A readily discerned doublet was recorded at 740 to 720cm.$^{-1}$.

The PMR spectrum ($CDCl_3$) showed a slightly distorted triplet centered at δ=4.80, and a very strong absorption at δ=1.30 with a noticeable shoulder on its low frequency side at δ=1.70. A poorly resolved multiplet near δ=0.95 was partially overlapped with the strong signal at δ=1.30.

For further analytical investigations a portion of the product was twice recrystallized from a diethyl ether-ethanol mixture, prepared as above (20ml./g. trimer), and dried at room temperature for 14 hrs. and

0.1mm. Hg. The product was further dried at room temperature for 24 hrs. and 20mm. Hg. The recovery after two recrystallizations was 50%.

Anal. Calcd. for $C_{27}H_{54}O_3$: C, 75.99%; H, 12.76%. Found: C, 75.83%; H, 12.71%. The capillary melting point was 36°C.

2. 2,4,6-Tri-n-nonyl-1,3,5-trioxane (decanal cyclic trimer).

a. Preparation in diethyl ether-pentane with $SbCl_5$ catalyst.

A 50ml. three-necked round-bottomed microglass flask containing a magnetic stirring bar, fitted with a pressure equalized addition funnel, a ground glass stopper, and a rectangular adapter with stopcock, served as the reaction vessel. The apparatus was assembled hot and cooled under a blanket of dry N_2 via the adapter. Diethyl ether (15ml.) was introduced into the addition funnel and diluted to a volume of 30ml. with n-pentane under a stream of dry N_2. The solvent mixture was delivered to the flask, the flask was immersed in an ice bath, and the stirrer was started. Decanal (8.5ml., 0.05 mole), distilled once, was introduced via syringe into the addition funnel under a stream of dry N_2.

After a period of 30 min. the flask stopper was momentarily raised and antimony pentachloride (0.5ml., 0.004 mole) was pipetted into the flask under a stream of dry N_2. The contents of the flask appeared slightly cloudy. The charge of decanal was then delivered to the reaction flask over a period of 1 min. and the contents of the flask developed a faint pink-brown tint. Within 5 min. after the delivery of the aldehyde was complete the reaction mixture transformed into an essentially solid mass. The stiff semisolid mass was turned out onto a fritted funnel with suction, and washed with a diethyl ether-ethanol

mixture (1 volume of diethyl ether diluted to 2.5 times its volume with ethanol) (3x20ml.). The solid product was dried on the filter for 20 min. and then dried overnight at room temperature and reduced pressure (20mm. Hg). Yield 6.6g. (95%).

The infrared spectrum (KBr) (pg. 255) showed a series of strong absorptions in the region of 3000 to 2800cm.$^{-1}$ (2975-, 2940-, and 2875-cm.$^{-1}$; ν_{as} and ν_s; CH_2 and CH_3). A strong absorption was also recorded at 1470cm.$^{-1}$ (δ_s; CH_2). A complex series of peaks was also recorded in the region of 1400 to 1200cm.$^{-1}$ with sharp predominant peaks at 1390 and 1370cm.$^{-1}$ ($\delta_s CH_3$; τ, ωCH_2). Strong absorptions were also recorded at 1160 and 1120cm.$^{-1}$. A sharp band was recorded at 720cm.$^{-1}$ which had a pronounced shoulder at 740cm.$^{-1}$.

The PMR spectrum ($CDCl_3$) (pg. 263) showed a triplet at δ=4.85, a strong single line centered at δ=1.25 with a shoulder on its low field side at δ=1.60, and an unresolved multiplet at δ=0.85 which overlapped the strong absorption at δ=1.25.

For further analytical investigations the trimer was twice recrystallized from a diethyl ether-ethanol mixture (30ml./g. trimer), prepared by diluting a volume of diethyl ether to 2.5 times its volume with ethanol. The recrystallized trimer was dried for 14 hrs. at room temperature and 0.1mm. Hg, then for 24 hrs. at room temperature and 20mm. Hg. The recovery from two recrystallizations was 50%.

Anal. Calcd. for $C_{30}H_{60}O_3$: C, 76.86%; H, 12.90%. Found: C, 76.79%; H, 12.89%.

3. 2,4,6-Tri-n-decyl-1,3,5-trioxane (undecanal cyclic trimer).

a. Preparation in diethyl ether-pentane with $SbCl_5$ catalyst.

A 50ml. three-necked round-bottomed microglass flask containing a magnetic stirring bar, fitted with a pressure equalized addition funnel, a ground glass stopper, and a rectangular adapter with stopcock, served as the reaction vessel. The apparatus was assembled hot from the oven and cooled under a blanket of dry N_2 via the adapter. Diethyl ether (15ml.) was introduced into the addition funnel and diluted to a volume of 33ml. with n-pentane under a stream of dry N_2. The solvent mixture was delivered to the flask, the flask was immersed in an ice bath and the stirrer was started. Freshly distilled undecanal (8ml., 0.04 mole) was introduced via syringe into the addition funnel under a stream of dry N_2.

After a period of 30 min. $SbCl_5$ (0.5ml., 0.004 mole) was pipetted into the flask under a stream of dry N_2. The contents of the flask appeared to be slightly cloudy. The charge of undecanal was delivered to the flask over a period of 1 min. and the reaction mixture developed a rust red tint. Within 5 min. the reaction mixture transformed into an essentially solid mass. The addition funnel was replaced with a ground glass stopper, the stopcock of the rectangular adapter was closed, the apparatus was disconnected from the N_2 source and stored overnight in the freezer (-15°C).

The flask was removed from the freezer and the flask and its contents were allowed to warm to room temperature. n-Pentane (10ml.) and 10% aq NaOH (2ml.) were added to the flask and the thick, red-brown tinted sludge was manually stirred for 15 min. with a glass rod. The stiff, semisolid mass was filtered through a fritted funnel, with suction. The product was washed in the funnel with chilled ethanol

(3x20ml.), dried on the funnel for 1 hr., and transferred to a 125ml. Erlenmyer flask. Crude yield 6.3g. (95%).

Chloroform (60ml.) was then introduced into the Erlenmyer flask and a two phase system resulted. The upper, minor, $CHCl_3$ poor phase was slightly cloudy and appeared to contain a small amount of undissolved solid. The contents of the flask were transferred to a 125ml. separatory funnel and were washed with two 20ml. portions of a 2% aqueous NaOH solution. The separatory funnel was copiously rinsed with distilled water between washings. The $CHCl_3$ rich layer, returned to the separatory funnel, was then washed with two 20ml. portions of distilled water. The lower, cloudy organic layer was drawn off from the upper, clear aqueous layer into a 125ml. Erlenmyer flask.

A sufficient amount of Drierite was added to the flask to form a layer of ca. 0.5cm. depth across the bottom of the flask. The flask was securely stoppered and the flask was swirled by hand for 5 min. then set aside for 4 hrs. at room temperature.

The supernatant liquid was separated by gravity filtration into a 125ml. Erlenmyer flask. The solid drying agent entrapped in the filter was rinsed with two 10ml. portions of $CHCl_3$, the washings being collected in the same flask which contained the original filtrate. The flask was securely stoppered and stored overnight in the refrigerator (5^oC).

The flask was removed from the freezer and the flask and its contents were allowed to warm to room temperature. The contents of the flask was then evaporated to ca. 1/2 its initial volume on a water bath (50^oC) and the flask was then removed from the water bath

and the flask and its contents were allowed to cool to room temperature. The resulting concentrated mixture was poured into a volume (40ml.) of acetone contained in a 125ml. Erlenmyer flask and the flask was then swirled by hand in an ice bath.

The resulting precipitate was recovered by suction filtration of the suspension, washed with acetone (4x20ml.), dried on the filter for 1 hr., and dried overnight at room temperature and reduced pressure (20mm. Hg). Yield 5.8g. (92%).

The infrared spectrum showed a series of strong absorptions in the region of 3000 to 2800cm.$^{-1}$ (2975-, 2925-, 2860-cm.$^{-1}$; ν_{as} and ν_{s}; CH_2 and CH_3). A strong absorption was also recorded at 1470cm.$^{-1}$ (δ_{s}; CH_2) which had notable shoulders at 1460 and 1440cm.$^{-1}$. A complex series of absorptions was recorded in the region of 1400 to 1200cm.$^{-1}$, the most predominant peaks of which were at 1380 and 1360cm.$^{-1}$. Strong absorptions were also recorded at 1160 and 1120cm.$^{-1}$. A moderate sharp band was recorded at 720cm.$^{-1}$, which had a shoulder at 740cm.$^{-1}$.

The PMR spectrum ($CDCl_3$) (pg. 264) showed a triplet centered at δ=4.80. (O-(R)C<u>H</u>-O). A strong single absorption was recorded at δ=1.25 (-(C<u>H</u>$_2$)$_x$-) which had a shoulder on its low field side atδ=1.5 (-C<u>H</u>$_2$-CHO-). An unresolved multiplet was recorded centered at δ=0.85 (C<u>H</u>$_3$-) which overlapped with the tail of the strong absorption at δ=1.25.

For further analytical investigations the trimer was twice recrystallized from a diethyl ether-ethanol mixture (30ml./g. trimer), prepared by diluting a volume of diethyl ether to 2.5 times its volume with ethanol. The trimer was dried for 14 hrs. at room temperature at

0.1mm Hg, then overnight at room temperature and 20mm. Hg. The recovery after two recrystallizations was 50%. Capillary melting point, 54-57°C. Literature melting point[121], 48°C.

Anal. Calcd. for $C_{33}H_{66}O_3$: C, 77.58%; H, 13.02%. Found: C, 77.61%; H, 12.98%.

4. 2,4,6-Tri-n-undecyl-1,3,5-trioxane (dodecanal cyclic trimer).

a. Preparation in diethyl ether-pentane with $SbCl_5$ catalyst.

A 50ml. three-necked round-bottomed microglass flask containing a magnetic stirring bar, fitted with a pressure equalized addition funnel, a ground glass stopper, and a rectangular adapter with stopcock, served as the reaction vessel. The apparatus was assembled hot from the oven and cooled under a blanket of dry N_2 via the adapter. Diethyl ether (15ml.) was introduced into the addition funnel and diluted to a volume of 30ml. with n-pentane under a stream of dry N_2. The flask was immersed in a cool water bath (10°C), the solvent mixture was delivered to the flask, and the stirrer was started. Freshly distilled dodecanal (10ml., 0.04 mole) was then introduced via syringe into the dropping funnel under a stream of N_2.

After a period of 20 min. $SbCl_5$ (0.8ml., 0.006 mole) was pipetted into the flask. The contents of the flask became slightly cloudy and a very small amount of a fine white solid was observed suspended in the solvent mixture. The entire charge of dodecanal was delivered to the flask over a period of 1 min., only a very slight coloration of the reaction mixture was observed. After 10 min. the water bath was removed and magnetic stirring of the reaction mixture was continued for 1.5 hrs.. During this period the clear reaction mixture gradually

developed a yellow brown tint. The addition funnel was replaced with a ground glass stopper, the stopcock of the rectangular adapter was closed, and the apparatus was disconnected from the N_2 source and stored in the freezer (-15°C) for 5 days.

The cold reaction mixture appeared as a three phase system; a small yellowish liquid upper layer, a voluminous white slush middle layer, and a very small dark yellow oil lower layer. The cold reaction mixture was suction filtered, the recovered solid was washed with a 9:1 acetone/water mixture (4x10ml.) and dried on the filter for 1 hr.. The solid product was transferred to a crystallizing dish (1.9g., 23%) and dried overnight at room temperature and reduced pressure.

The infrared spectrum (KBr) (pg. 256) showed strong absorptions in the region of 3000 to 2800cm.$^{-1}$ (2960-, 2925-, and 2860cm.$^{-1}$; ν_{as} and ν_s, CH_3 and CH_2). A moderately strong absorption band, with several shoulders, was recorded at 1470cm.$^{-1}$ (δ_s; CH_2), a much weaker band was recorded at 1360cm.$^{-1}$. Two moderately strong absorptions were recorded at 1160 and 1120cm.$^{-1}$ (C-O-C stretching). A band was recorded at 720cm.$^{-1}$ which had a shoulder at 740cm.$^{-1}$.

The PMR spectrum ($CDCl_3$) (pg. 265) showed a weak triplet near δ=4.80 (O-(R)C<u>H</u>-O). A strong single absorption centered at δ=1.25 ((C<u>H</u>$_2$)$_x$) with a small shoulder atδ=1.50 (-C<u>H</u>$_2$-CHO-) was recorded. An unresolved multiplet, centered atδ=0.85 (C<u>H</u>$_3$), was also recorded.

The inherent viscosity of a 0.5g./dl. solution of the trimer in tetralin at 31°C was η=0.03dl./g..

For further analytical investigations the trimer was twice recrystallized from a diethyl ether-ethanol mixture (30ml./g. trimer)

prepared by diluting a volume of diethyl ether to 2.5 times its volume with ethanol. The trimer was dried for 14 hrs. at room temperature at 0.1mm. Hg, then overnight at room temperature and 20mm. Hg. The recovery after two recrystallizations was 50%. Capillary m.p., 60-63°C. Literature melting point[121], 61.5°C.

Anal. Calcd. for $C_{36}H_{72}O_3$: C, 78.19%; H, 13.12%. Found: C, 77.62%; H, 12.95%.

F. Extraction of LTB with MCH and Analysis of the Extract

A Soxhlet extraction apparatus, topped with an Allihn type condenser was used in this experiment. The top of the condenser was connected, via a glass tee, to a source of dry N_2 and a paraffin oil bubbler. The outlet of the bubbler was protected with a drying tube filled with a mixture of calcium chloride and soda lime. The extractor and condenser were assembled hot and cooled with a N_2 purge for 1 hr.. The bottom of the extractor was then fitted with a 250ml. round-bottomed flask containing methylcyclohexane (200ml.) and a few small pieces of silicon carbide. The condenser was momentarily raised and a stainless steel mesh extraction thimble containing crude LTB (8.8g., 0.11 mole) was placed into the extractor chamber. A sample of the crude LTB employed gave a 45-50% yield of sublimate in 12 hrs. when sublimed at 130° (0.1mm. Hg). The crude LTB was extracted overnight, estimated number of cycles; 15. When the extractor had drained to complete the last cycle the heating of the pot was discontinued and the apparatus and its contents were allowed to cool to room temperature. During this interval a very small amount of solid material in the yellowish

MCH extract settled out.

The flask containing the MCH extract was removed from the extraction apparatus and three 20ml. aliquots of the methylcyclohexane were pipetted into separate 125ml. Erlenmyer flasks. A syringe needle connected to a source of dry N_2 and extending through the open neck of the extractor pot or the Erlenmyer flask was used to maintain an atmosphere of N_2 over the extract solution during its transfer.

Distilled water (10ml.) was then added to each of the Erlenmyer flasks, the flasks were securely stoppered and swirled by hand for 5 min.. The contents of each flask was, in turn, transferred to a separatory funnel. The aqueous layer was drawn off into a clean receptacle and the organic layer was washed with two additional 10ml. portions of distilled water. All water washings of one individual aliquot of the extract solution were collected in the same receptacle. Each of the three sets of combined water washings were then titrated with 1.000N HCl, which was previously standardized against Na_2CO_3. One set of combined water washings was titrated potentiometrically, the other two sets of combined water washings were titrated to a methyl orange endpoint. The number of equivalents indicated by the potentiometric titration was 0.00458, the number of equivalents indicated by the two colorimetric titrations was, respectively, 0.00465 and 0.00459. These data gave a value of 0.23M for the concentration of the MCH extract solution indicating that 42% of the original sample of LTB was extracted by MCH. A value of 43% was obtained in a duplicate experiment.

The entire experiment was repeated using a portion of a commercial

sample of LTB, taken from a freshly opened bottle, which gave an 85% yield of sublimate. Titration of the extract, as above, indicated that 90% of the LTB was extracted by MCH.

G. Polyhexanal [Poly((2-n-pentyl)oxymethylene)]

The hexanal used in this experiment was distilled once and stored over molecular sieves (3A) for 14 hrs. prior to its use. A 500ml. three-necked round-bottomed flask, fitted with a paddle type stirrer and glass bushing, a rectangular adapter, and a reducing adapter closed with a serum stopper, served as the polymerization vessel. The flask was flamed out and stored in the oven until needed. The apparatus was assembled hot from the oven and cooled under a blanket of dry N_2 via the adapter. The flask was then charged, via syringe, under N_2, with MCH (90ml.) and a volume (5ml.) of a 0.63M solution of LTB in MCH (0.0031 mole LTB). The stirrer was started and the flask was immersed in a -78^{o}C cold bath contained in Dewar vessel. The rate of addition of the aldehyde was such that the entire charge (20ml., 0.16 mole) was introduced over a 5 min. period. The polymerization mixture was difficult to observe in the flask immersed in the cold bath, however, the development of a blue-white tint and thickening of the polymerization mixture was noted.

A clean dry test tube, closed with a serum stopper, was purged with dry N_2 (syringe needle inlet and outlet) for 10 min.. The tube was then charged, via syringe, under N_2, with MCH (5ml.) and hexanal (1ml., 0.007 mole). The blank tube was immersed in the same cold bath as the polymerization vessel and was periodically removed for inspection.

After a period of 4 hrs. the stirrer was stopped, and the Dewar vessel was packed well with CO_2(s). The polymerization vessel and its contents were allowed to stand overnight at -78°C.

While vigorous agitation of the polymerization mixture was maintained the flask was charged with 100ml. of a chilled 4:1 mixture of acetic anhydride and pyridine. The flask was kept immersed in the cold bath for 10 min. and the cold bath was then gradually removed so that the flask and its contents warmed to room temperature in 30 min.. The stirrer was stopped and the reaction mixture, which contained gel like particles, segregated into two phases. The serum stopper closed adapter was removed and, while a strong stream of N_2 was maintained over the reaction mixture, a small aliquot (ca. 10ml.) of the upper layer was drawn up into a syringe (prechilled by rinsing with -78°C acetone) and delivered to a beaker containing 20ml. of well stirred ice cold acetone which produced a suspension. Acetone (50ml.) was added, with stirring, to the flask containing the reaction mixture. The open neck of the flask was fitted with a Claisen distilling head fitted with a short (ca. 13cm.) column, a thermometer, and a collection adapter which was fitted with a 150ml. round-bottomed flask. The receiver flask was immersed in an ice bath. The reaction flask was then immersed in a 60°C oil bath and the temperature of the oil bath was increased to 120°C over a 20 min. period. In this interval the temperature at the top of the short column rose to 55°C and ca. 30ml. of volatiles was collected. The temperature at the top of the column gradually rose to 85-90°C and the volume of volatiles collected increased to ca. 70ml. over a period of 30 min..

When a total of ca. 100ml. of volatiles had been collected (15 additional min.) the stirrer was stopped and the distillation assembly was removed. The hot reaction mixture was suction filtered, in two portions, through a hot (110^{o}C) coarse fritted funnel. When the filtration was nearly complete acetone (20ml.) and distilled water (5ml.) were added to the funnel.

The product was transferred to a mortar and was broken up and ground with acetone and a small amount of distilled water. The acetone-water mixture was decanted and replenished several times during the grinding procedure. During the grinding procedure the product gradually became whiter, opaque, and brittle. The ground product was transferred to a coarse fritted funnel, washed with acetone (3x40ml.), a 5:1 mixture of acetone and water (2x40ml.), again with acetone, then dried on the filter for 1 hr..

The suspension of the product isolated before the end capping reaction was complete was suction filtered through a medium fritted funnel. The collected product was copiously washed with acetone (200ml. total) followed by a 5:1 mixture of acetone and water (50ml. total), and finally washed again with acetone. The product was then dried on the filter for 1 hr.. The crude yield of the more completely capped sample (designated A) was 6.6g. (40%). The crude yield of the less completely capped sample (designated B) was 1g. (6%). Both products were then dried overnight at room temperature and 0.1mm. Hg over KOH. Product B was softer and deteriorated at much faster rate than product A. The thermogravimetric curves obtained at 20^{o}C/min. for the two products were compared.

The infrared spectrum (neat) (pg. 256) showed strong absorptions at 2920cm.$^{-1}$ (shoulder at 2960cm.$^{-1}$) and 2850cm.$^{-1}$ (ν_{as}; CH_3, ν_{as} and ν_s; CH_2). A weak absorption was recorded near 1730cm.$^{-1}$ (ν C=O). Moderate absorptions were recorded at 1470cm.$^{-1}$ (δ_s; CH_2) (shoulders at 1460 and 1440cm.$^{-1}$) and 1380cm.$^{-1}$ (shoulders at 1370 and 1360cm.$^{-1}$) (C-H bending). A moderate sharp band was recorded at 1140cm.$^{-1}$ as was a strong sharp band at 1120cm.$^{-1}$. A weak, broad absorption was recorded near 720cm.$^{-1}$.

Anal. (prod. A) calcd. for $(C_6H_{12}O)_n$: C, 70.95%; H, 12.11%. Found: C, 70.85%; H, 12.10%.

The products were stored at room temperature and reduced pressure and thereafter at room temperature open to the atmosphere.

H. Polynonanal [Poly((2-n-octyl)oxymethylene)]

1. Attempted exploratory scale polymerization of undistilled nonanal in MCH with LTB initiator. Two dry 20x150mm. test tubes, closed with serum stoppers, were alternately evacuated to ca. 20mm. Hg and then filled with dry N_2 via a hypodermic syringe needle. This cycle was repeated three times. The tubes were then charged, via hypodermic syringe, with MCH and then nonanal, which had been pretreated with $Na_2CO_3 \cdot H_2O$ and CaH_2 as described. The charge of the first tube (tube A) was; MCH (22ml.) and nonanal (2.3g., 0.014 mole). The charge of the second tube (tube B) was; MCH (21ml.) and nonanal (3.29g., 0.023 mole).

The tubes were cooled to -20°C in an ice-salt mixture and then charged with a 0.63M solution of LTB in MCH. The charge of initiator solution in tube A was 0.5ml. (0.00031 mole, ca. 2 mole %). The charge of initiator solution in tube B was 0.8ml. (0.00050 mole, ca. 2 mole %).

The tubes were vigorously shaken and then returned to the -20°C bath for 30 min.. The tubes were then placed in a bath maintained at -78°C and contained in a Dewar vessel and the tubes were allowed to stand overnight at -78°C. At the time the initiator was charged the contents of tube A consisted of a clear solution whereas a small amount of flaky white solid precipitate was observed in tube B.

In a separate experiment, conducted at the same time, a clean dry 15x125mm. test tube, closed with a serum stopper, was purged with dry N_2 (syringe needle inlet and outlet) for 10 min.. The tube was then charged with toluene (3ml.) and chloral (5ml.) and the tube was then placed in an oil bath maintained at 70°C. After 10 min. the tube was then charged with 1.6ml. of the 0.63M solution of LTB in MCH. The tube was vigorously shaken and then immersed in an ice bath. Within 5 min. the contents of the control tube had transformed into a solid white plug.

After the tubes containing the nonanal polymerization mixtures were allowed to remain overnight at -78°C the contents of tube A were completely fluid. The contents of tube B was a very thick slurry of fine white particles. Each tube was then charged, via syringe and under N_2, with 1ml. of a 3:2 mixture of acetic anhydride/pyridine which had been chilled to below -50°C. The tubes were vigorously shaken and returned to the -78°C bath. After a period of 1 hr. the tubes were placed in a -20°C ice-salt bath. After a period of 2 hrs. the contents of both tube A and tube B were homogeneous. The tubes were opened and the contents of each was added to an approximately equal volume of a 3:1 mixture of methanol and dimethylacetamide. The

clear, one phase, homogeneous systems which resulted were not further characterized.

2. Attempted exploratory scale polymerization of nonanal in n-hexane with LTB initiator. A clean dry 25ml. volumetric flask, closed with a serum stopper, was charged, via syringe and under N_2, with freshly distilled nonanal (2.381g., 0.0168 mole) and the volume was made up with n-hexane. The concentration of the resulting mother solution was taken to be 0.669M in nonanal.

Six clean dry 15x125mm. test tubes, closed with serum stoppers, were alternately evacuated to ca. 20mm. Hg and filled with dry N_2 via a hypodermic syringe needle. This cycle was repeated three times. The tubes were then divided into two groups (A and B) and charged, via syringe and under N_2, with a volume of the mother solution and a volume of n-hexane according to the following schedule.

Tube:	A1	A2	A3	B1	B2	B3
ml. mother solution	4.0	2.6	2.0	6	3	1
approximate # of moles of aldehyde x 10^3	2.7	1.7	1.3	3.9	1.9	0.66
ml. n-hexane	0	3	6	0	3	6
ml. 0.08M LTB solution	1.6	1.3	1.8	2.4	1.3	0.4
approximate mole% LTB	9.7	6.1	11	4.9	5.5	4.8

The tubes were all then immersed in an ice-salt bath (-18° to 22°C). The tubes were then each charged with a volume of 0.08M solution of LTB in MCH. The tubes were then vigorously shaken and returned to the ice-salt bath.

In a separate control experiment, conducted concurrently, a clean

dry 15x125mm. test tube, closed with a serum stopper and treated as above, was charged under N_2 with n-hexane (1ml.) and chloral (3ml.). The tube was then placed in an oil bath maintained at 70°C. After a period of 5 min. the tube was charged with 3.5ml. of the 0.08M LTB solution, shaken and immersed in the ice-salt bath. Within 3 min. the contents of the tube had transformed into a solid, opaque white plug with a ca. 2mm. layer of clear supernatant liquid.

After a period of 1 hr. the tubes containing the nonanal polymerization mixtures were removed from the ice-salt bath and placed in a -78°C bath contained in a Dewar vessel. At the time of the transfer to the -78°C bath the contents of all the tubes, except for tube A1, were clear and homogeneous. A small amount of granular white precipitate was observed in tube A1. The tubes were stored overnight in the -78°C bath. The contents of tube A1 appeared to be a solid white plug. The appearance of the contents of the remaining tubes was quite similar. The relative amount of granular solid roughly paralleled the initial monomer concentration.

Five tubes were each charged, via syringe and under N_2, with 2ml. of a chilled 1:1 mixture of acetic anhydride/pyridine. Addition of this mixture to the reaction mixture appeared to cause some coagulation of the precipitate. The tubes were allowed to remain in the -78°C bath for a period of 1 hr. and were then transferred to a -20°C ice-salt bath where they were allowed to remain for a period of 2 hrs.. After this time the contents of tubes A1 and B3 were homogeneous and the contents of each of the two tubes were poured into an approximately equal volume of a well stirred, chilled (0°C) mixture of methanol and

dimethylacetamide (1:1). No characterization of the resulting mixtures of two liquid phases was attempted.

The contents of tubes A2, A3 and B2, which were all slightly cloudy, were suction filtered while cold through individual medium fritted funnels. Filtration of the contents of tubes A2 and B2 gave products; A3 gave no product.

The product from the filtration of the tube A2 was rinsed into a test tube with CH_2Cl_2 which appeared to dissolve the polymer. A very thin film was deposited on the side of the test tube as the solvent evaporated.

The product from the filtration of the contents of tube B2 was placed into a small test tube. Deuterated chloroform was added to the test tube which dissolved the solid from the spatula. The PMR spectrum of the cloudy solution was recorded. The solution was very dilute and only a broad signal, centered near δ=1.30, could be distinguished.

3. Preparative scale polymerization of nonanal in MCH with LTB initiator. A 250ml. three-necked round-bottomed flask, fitted with a paddle type stirrer, a rectangular adapter, and a reducing adapter closed with a serum stopper and fitted with a Teflon sleeve, served as the polymerization vessel. The apparatus was assembled hot and cooled under a blanket of dry N_2 via the adapter. The flask was then charged, via syringe and under N_2, with MCH (72ml.) and 8ml. of a 0.625M solution of LTB in MCH (0.005 mole LTB). The flask was then immersed in a low temperature bath, contained in a Dewar vessel, which was maintained at -58° to -60°C by judicious addition of small quantities of finely crushed CO_2(s). After a period of 30 min. the flask was charged

with twice distilled nonanal (8ml., 0.046 mole). After a period of 15 min. the contents of the flask appeared as a viscous liquid containing a modest amount of suspended white material; agitation of the reaction mixture was still possible. The bath temperature was brought to -78°C and the Dewar vessel was packed well with CO_2(s). After a period of 15 min. the stirrer was stopped and the flask and its contents were allowed to stand overnight at -78°C.

The stirrer was re-started and the polymerization mixture was agitated for 2 hrs. while the flask was kept immersed in the -78°C bath. The flask was then charged, via syringe and under N_2, with 100ml. of a chilled 4:1 mixture of acetic anhydride/pyridine while vigorous agitation of the reaction mixture was maintained. After 15 min. the cold bath was slowly removed in several steps requiring 15 min. to complete. The vigorous agitation of the viscous reaction mixture was continued for a period of 1 hr. as the flask and its contents warmed to room temperature. A suspension of small particles formed in the flask.

The reducing adapter with serum stopper closure was quickly removed and replaced with a Claisen distilling head fitted with a short (ca. 13cm.) column holding a thermometer and fitted with a collection adapter which held a 100ml. round-bottomed flask. The receiver flask was immersed in an ice bath. The reaction vessel was then gradually immersed in an oil bath maintained at 100°C. A period of 35 min. was required to raise the surface of the oil bath to the level of the contents of the flask. During this time ca. 15ml. of volatiles was collected, the reaction mixture developed a yellow brown tint, and the particles of solid material in the reaction mixture became highly

swollen and less distinct. The temperature of the oil bath was raised to 125°C over a period of 15 min. and was then maintained at that temperature for 30 min.. A total volume of ca. 100ml. of volatiles was collected. The hot reaction mixture was suction filtered through a warm (70°C) 60ml. coarse fritted funnel. The solid product collected in the funnel was washed with three 30ml. portions of a 1:1:2 mixture of acetic acid/acetone/diethyl ether. The filtration was very slow and the filtration and washing required a period of 1.5 hrs.. The waxy, crumbly plug of the product was broken up with a spatula and suspended in the filter with 50ml. of a 3:1 mixture of acetone and water. The liquid was drawn off with suction and the suspension-drain procedure was repeated. The product was finally washed with three 20ml. portions of acetone and dried on the filter for 2 hrs.. The product was transferred to a crystallizing dish (crude yield 2.3g., 35%) and dried overnight at room temperature and reduced pressure (0.5mm. Hg) over KOH.

The white crumbly product was soluble in $CHCl_3$. However, the extent and completeness of the dissolution was difficult to determine in as much as the product formed clear, very highly swollen particles with even a small amount of $CHCl_3$. Chloroform solutions of the product of greater than 0.2g./dl. concentration were so slowly suction filtered that significant evaporation of the solvent occurred during the filtration.

The infrared spectrum of a film of the product (from $CHCl_3$) (pg. 257) showed very strong absorptions at 2925 and 2875cm.$^{-1}$ (ν_{as} and ν_s; CH_2). Moderate to strong absorption bands, with several shoulders, were recorded at 1470 and 1380cm.$^{-1}$ (C-H bending). A strong band was

recorded at 1120cm.$^{-1}$ which had a noticeable shoulder near 1140cm.$^{-1}$ (C-O stretch). A weak absorption was recorded near 740cm.$^{-1}$. No absorptions assignable to OH or C=O groups in the product were observed.

The PMR spectrum ($CDCl_3$) (pg. 266) showed a weak, broad absorption in the region of δ=5.05-4.55 (O-(R)C<u>H</u>-O). A strong single absorption signal was recorded at δ=1.25 (-(C<u>H</u>$_2$)$_x$-). An unresolved multiplet, which partially overlapped the strong signal at δ=1.25, was recorded near δ=0.85 (-C<u>H</u>$_3$).

A sample of the polymer (0.51g.) was placed into a test tube together with a small amount of ethanol and the sample was ground with the ethanol in the test tube with the end of a glass rod. A volume (3ml.) of 2,4-dinitrophenylhydrazine reagent, prepared according to Vogel[122] was added to the test tube which was then agitated while being heated in a 60^{o}C water bath. Within a period of 5 min. the contents of the test tube transformed into a thick slurry of yellow solid. The solid 2,4-dinitrophenylhydrazone was isolated by suction filtration of the slurry, washed with ethanol, and dried on the filter for 1 hr. (crude yield 0.96g., nearly quantitative). The hydrazone was then recrystallized from ethanol and dried for 14 hrs. at reduced pressure (0.1mm. Hg) (m.p.=101-102^{o}C, m.p. lit.[123] 100^{o}C).

The inherent viscosity of a 0.59g./dl. solution of the polymer in tetrahydronapthalene (tetralin) (contg.<0.05% N,N'-di-β-napthyl-p-phenylenediamine) at various temperatures was (T, η(dl./g.)); 35^{o}C, 1.48; 46^{o}C, 1.36; 57^{o}C, 1.06; 66^{o}C, 1.06. The tetralin solution had a faint haze which was not removed by pressure filtration (N_2 pressure) of the warm (60^{o}C) solution through a coarse fritted funnel.

Anal. Calcd. for $(C_9H_{18}O)_n$: C, 75.99%; H, 12.95%. Found: C, 75.39%; H, 12.61%.

A portion of the polymer was reprecipitated from $CHCl_3$. Polymer (1.5g.) was placed into a 50ml. Erlenmyer flask. Chloroform (30ml.) was then added to the flask and the flask was securely stoppered and allowed to stand overnight at room temperature. A clear, thick uniform gelatinous mass was observed as a layer on top of the $CHCl_3$ in the flask. The flask was vigorously shaken to disperse the highly swollen mass. A magnetic stirring bar was placed into the flask and the contents of the flask were magnetically stirred for 5 hrs. at room temperature. The contents of the flask were then added to 50ml. of well stirred, cold (0^oC) acetone contained in an Erlenmyer flask which was affixed in an ice bath. The resulting suspension was suction filtered through a coarse fritted funnel. The white recovered polymer was washed with acetone (2x20ml.), dried on the filter for 1 hr., then dried for 5 hrs. at room temperature and reduced pressure (0.5mm. Hg) (1.1g., 73% recovery).

A small amount (ca. 0.1g.) of solid was also recovered from the mother liquor by cooling the mother liquor to -20^oC and suction filtration of the resulting suspension through a medium fritted funnel.

The infrared spectrum of films (from $CHCl_3$) of each fraction (pg. 257) were essentially identical to each other excepting that in the spectrum of the more soluble fraction, obtained by cooling of the mother liquor, a more pronounced absorption in the region of 1730cm.$^{-1}$ was recorded. The spectra were better resolved than the spectrum originally obtained and also showed an absorption near 1570cm.$^{-1}$

($\nu_{C=O}$ CO_2^- ?) not recorded in the initial spectrum.

4. Preparative scale polymerization of nonanal in MCH with LTB initiator using a controlled temperature program. A flamed out 250ml. three-necked round-bottomed flask fitted with a paddle type stirrer and glass bushing, a Teflon thermometer adapter fitted with a short length of glass rod, and a ground glass joint fitted with a 3-way stopcock, served as the polymerization vessel. The apparatus was treated as described in section D.1..

The flask was charged, via syringe and under N_2, with MCH (100ml.) and a volume (4ml.) of a 0.88M solution of LTB in MCH (0.0035 mole LTB) and the mechanical stirrer was started. The polymerization vessel was then immersed in a -20°C cooling bath contained in a Dewar vessel which was fitted with an electrically controlled liquid N_2 cooling coil.

After a period of 20 min. the flask was charged, via syringe and under N_2, with twice distilled nonanal (20ml., 0.12 mole). After a period of 5 min. the temperature of the bath was gradually and continuously lowered to -30°C over a period of 30 min. and the temperature of the bath was maintained at -30°C for a period of 15 min. The bath temperature was then gradually and continuously lowered to -50°C over a period of 30 min.. As the bath temperature approached -50°C the formation of a precipitate was observed in the polymerization mixture. The precipitate was first observed as nearly transparent, blue tinted clumps. As the bath temperature was lowered to -55°C (10 min.) the reaction mixture became more viscous and difficult to stir. The bath temperature was then brought to -78°C in 10 min.. The Dewar vessel was packed well with solid CO_2, the stirrer was stopped, and the flask and

its contents were allowed to stand overnight at -78°C.

The stirrer was restarted and after a period of 2 hrs. the flask was charged, via syringe and under N_2, with a chilled mixture of acetic anhydride (60ml., 0.64 mole) and pyridine (10ml., 0.12 mole). After a period of 10 min. the cold bath was gradually removed and the mixture slowly warmed to room temperature over a period of 1.5 hrs.. After an additional period of 1 hr. the stirring was stopped and the reaction mixture was suction filtered, in several portions, through a 60ml. coarse fritted funnel. The initially rapid filtration rate quickly dropped off. Addition of acetone to the contents of the filter aided the filtration slightly. Acetone (100ml.) was added to the remaining unfiltered reaction mixture in the reaction flask, the flask was kept packed in ice during the filtration procedure.

The contents of the 60ml. funnel, together with 60ml. of acetone, was transferred to a 150ml. coarse fritted funnel and suction filtration was continued. The remaining reaction mixture was filtered in several portions. A volume (20-30ml.) of acetone was mixed with each portion of reaction mixture as it was poured into the funnel.

The vacuum to the filter flask was clamped off and the tacky, crumbly, translucent white product was broken up and suspended in acetone (50ml.) in the filter, the solvent was then drawn off with suction. This process was repeated with acetone (2x50ml.), a 5:1 mixture of acetone and water (2x50ml.) and finally with acetone (50ml.). The solid product, which became harder and more opaque with the washings, was dried on the filter for 1 hr. then transferred to a crystallizing dish. Crude yield of wet product; 15.6g. (95%). The

product was then dried overnight at room temperature and reduced pressure (25mm. Hg); yield after drying; 6.45g. (38%).

The infrared spectrum of a film (from $CHCl_3$) of the polymer (pg. 258) was very similar to that of the polynonanal sample prepared previously. A moderately narrow band of medium intensity was recorded near 2730cm.$^{-1}$ (ν_{CH}; RC<u>H</u>O) suggested that monomer present in the polymer was contributing the absorption near 1730cm.$^{-1}$. A weak, slightly broadened absorption band centered near 3425cm.$^{-1}$, not present when the spectrum of the "blank" NaCl plates was recorded, suggested the presence of OH endgroups or occluded water in the sample.

The PMR spectrum of the product ($CDCl_3$) (pg. 267) was identical to that recorded for the previous sample of polynonanal.

A portion of the product was reprecipitated from $CHCl_3$. A sample of the polymer (0.991g.) was weighed into a 50ml. Erlenmyer flask and a volume (10ml.) of $CHCl_3$ was added to the flask. An additional volume (20ml.) of $CHCl_3$ was added to the flask in several portions over a 2 hr. period during which time the polymer sample became highly swollen. A magnetic stirring bar was placed into the flask and the contents of the flask was magnetically stirred at room temperature for a period of 4 hrs. during which time an additional volume (10ml.) of $CHCl_3$ was added to the flask.

Acetone (5ml.) was added to the Erlenmyer flask and the mixture was pressure filtered (N_2 pressure) through a coarse fritted funnel into a clean, dry 50ml. Erlenmyer flask, a thin film was deposited on the interior surfaces of the funnel. The filtrate was then slowly poured into a well stirred volume (30ml.) of chilled (0^oC) acetone

contained in a 125ml. Erlenmyer flask. Polymer precipitated and was recovered by suction filtration of the suspension through a medium fritted funnel, washed with acetone (2x20ml.), and dried on the filter for 1 hr., (0.863g., 87% recovery). The reprecipitated polymer was further dried for 48 hrs. at room temperature and reduced pressure (25mm. Hg).

A small amount of the chloroform reprecipitated material was placed in a test tube together with one drop of conc. H_2SO_4. The solid immediately collapsed into a yellow oil. A volume (3ml.) of 2,4-dinitrophenylhydrazine reagent was then added to the test tube and the test tube was agitated in a 60°C water bath. The contents of the tube readily formed one phase and, almost instantaneously, transformed into a very thick slush. The 2,4-dinitrophenylhydrazone was isolated by suction filtration, washed with ethanol, and dried on the filter for 1 hr.. The bright yellow solid was recrystallized from ethanol (20ml.). The resulting mat of yellow needles was dried for 8 hrs. at room temperature and reduced pressure (m.p.=101-102°C, m.p. lit.[123] 100°C).

The major portion of polynonanal which was not reprecipitated from $CHCl_3$ was divided in half. One half portion was treated with several fresh portions of acetone (65ml./g. polymer) for 48 hrs. at room temperature. The polymer was recovered by suction filtration of the suspension, washed well with acetone, dried on the filter for 1 hr., then dried overnight at room temperature and 25mm. Hg.

The second half portion of the sample (2.5g.) was placed into a 250ml. Erlenmyer flask, together with 120ml. of toluene. The flask was securely stoppered and allowed to stand overnight at room

temperature. Toluene (25ml.) and distilled water (10ml.) were then placed into the flask and the contents of the flask were magnetically stirred for 8 hrs. at room temperature. The stirring was discontinued and the mixture was allowed to stand overnight at room temperature. The contents of the flask were then transferred to a separatory funnel and the lower aqueous layer was drawn off. The toluene layer was then added dropwise to 400ml. of chilled ($0^{o}C$) acetone contained in a 1 l. Erlenmyer flask which was affixed in an ice bath. A suspension of fibrous white polymer resulted which was then suction filtered through a medium fritted funnel. A coherent, off white, translucent, rubbery disk formed on the frit. The disk of polymer was rinsed with acetone and cut into numerous small pieces with a razor blade. The pieces were suspended in 60ml. of a 5:1 mixture of acetone and water. The suspension was suction filtered through a coarse fritted funnel. The recovered toluene reprecipitated polymer was washed with acetone (2x10ml.), dried on the filter for 1 hr., then dried for 3 hrs. at room temperature and 0.01mm. Hg. A portion of the toluene reprecipitated polymer was ground at low temperature ($T < -50^{o}C$) into a fine powder.

The infrared spectrum (pg. 258) of a film (from $CHCl_3$) of the toluene reprecipitated polymer was very similar to the spectrum recorded for the original material.

The number average molecular weight by VPO ($37^{o}C$ in $CHCl_3$) was ca. 17,000 ($DP_n \simeq 120$).

The inherent viscosity of a 0.41g./dl. solution of the polymer in tetralin (0.05% N,N'-di-β-napthyl-p-phenylenediamine) at $61^{o}C$ was; $\eta = 2.9$. The original solution was held at $60^{o}C$ for 4 hrs., cooled to room

temperature, and stored overnight at room temperature. A 5ml. aliquot of the solution was diluted to a volume of 10ml. with the tetralin solvent. The inherent viscosity of the resulting solution at 60°C was η=1.4.

Anal. Calcd. for $(C_9H_{18}O)_n$: C, 75.99%; H, 12.76%. Found: C, 75.46%; H, 12.49%.

5. Extrusion of polynonanal in a capillary rheometer. The acetone treated portion of the polynonanal described in section H.2. was extruded at 80°C through a tungsten carbide capillary in the capillary rheometer accessory of an Instron model TTCM (Instron Corporation, Canton, Ma.). The diameter of the capillary was 0.030" (0.762cm.) and its length was 1.0078" (2.559cm.).

The capillary was fitted to the end of the rheometer barrel, the rheometer was heated to temperature, and the polymer was loaded into the rheometer barrel and tamped with a brass rod. During the tamping procedure a number of very small fibrils were formed on the side of the tamping rod. The plunger [0.375" (0.953cm.) dia.] was inserted into the barrel and the plunger and sample were preheated for a period of 3 min.. During this preheat period a very small amount of material was extruded through the capillary under the weight of the plunger. The crosshead was lowered and connected to the plunger and the polymer was extruded at a crosshead speed of 0.5cm./min.. The force necessary to maintain a constant crosshead speed was recorded at a chart speed of 10cm./min. and a recorder range setting which corresponded to 100kg. for a full scale deflection of the recorder pen. A very smooth force trace was obtained. The apparent steady state viscosity was 3350 poise.

An odor of monomeric nonanal was detected in the vicinity of the rheometer.

The filament extrudate was moderately opaque and was easily broken by a force applied perpendicular to its long axis. The extrudate could easily support its own weight to a vertical height of at least 40cm.. The extrudate was seen to coil slightly before fracturing in the 2l. beaker which was used to collect the extrudate. Some permanent set of the bending occurred as the stiffness of the extrudate increased slightly as it cooled.

The filament extrudate was cut into a number of 10-20cm. pieces which were soaked in several fresh portions of acetone at room temperature for 3 hrs.. The filaments were stored in the freezer in tightly stoppered test tubes under fresh acetone until needed. The filaments were rinsed with a small volume of acetone, blotted dry, and dried in vacuo at room temperature before they were used.

During the cleaning of the rheometer a very thin translucent film was peeled from the side of the plunger. The infrared spectrum of the film was recorded (pg. 258). A strong, fairly broad absorption was recorded near 1720cm.$^{-1}$, suggesting that the film was highly contaminated with monomeric nonanal, probably formed by degradation of the polymer during the extrusion process.

I. Polydecanal [Poly((2-n-nonyl)oxymethylene)]

1. Preparative scale polymerization of decanal in MCH with LTB initiator. Decanal was distilled once and stored over molecular sieves (3A) for 14 hrs. prior to its use. A 250ml. three-necked round-

bottomed flask, fitted with a paddle type stirrer, a rectangular adapter, and a reducing adapter closed with a serum stopper and fitted with a Teflon sleeve, served as the polymerization vessel. The apparatus was assembled hot and cooled under a blanket of dry N_2 through the rectangular adapter.

The flask was then charged, with a syringe and under N_2, with MCH (60ml.) and 5ml. of a 0.7M solution of LTB in MCH (0.004 mole LTB). The stirrer was started and the flask was immersed in a low temperature bath contained in a Dewar vessel and maintained at -58°C to -60°C by judicious addition of small quantities of finely divided CO_2(s). After a period of 30 min. the flask was charged with decanal (13ml., 0.069 mole), the entire charge of aldehyde was delivered within a period of 0.5 min.. The reaction mixture was a thick white slurry. The temperature of the bath was then lowered to -78°C. After 5 hrs. the stirrer was stopped, the Dewar vessel was packed well with CO_2(s), and the flask was allowed to sit overnight at -78°C. The stirrer was restarted and, after 1 hr., a chilled mixture of acetic anhydride (85ml., 0.90 mole) was added to the polymerization mixture. After 15 min. the cold bath was gradually removed in such a way that the reaction flask and its contents warmed to room temperature in 30 min.. After an additional 20 min. the stirrer was stopped and the reaction mixture was poured, with stirring, into 150ml. of chilled (0°C) acetone. The resulting suspension was suction filtered through a medium fritted funnel and the collected solid product was washed with methanol (20ml.), acetone (2x20ml.), a 5:1 mixture of acetone and distilled water, again with acetone and dried on the filter for 1 hr.. The product was transferred

to a crystallizing dish (1.9g., 17%) and dried overnight at room temperature and 25mm. Hg (1.0g., 9%).

The infrared spectrum of a film (from $CHCl_3$) of the polymer (pg. 259) showed strong, broad absorptions in the region of 3250 to 2650cm.$^{-1}$. Two peaks could be identified at 2950 and 2850cm.$^{-1}$ (ν_{as} and ν_s; CH_2). A moderate to weak absorption was recorded at 1710cm.$^{-1}$ which had a broad shoulder near 1725cm.$^{-1}$ ($\nu_{C=O}$). Moderate to strong absorptions were recorded at 1470cm.$^{-1}$ (shoulders near 1460 and 1430cm.$^{-1}$) and 1370cm.$^{-1}$ (several shoulders) (C-H bending). A strong, broad absorption band was recorded from 1190 to 900cm.$^{-1}$ which had resolved shoulders at 1140 and 1120cm.$^{-1}$. An absorption was recorded near 730-cm.$^{-1}$ which had a small shoulder near 740cm.$^{-1}$.

The PMR spectrum ($CDCl_3$) indicated that the polymer was unstable because it was contaminated with carboxylic acid as indicated by a notable absorption near δ=10.5 ($CO_2\underline{H}$).

The inherent viscosity of a 0.5g./dl. solution of the polymer in tetralin (0.05% N,N'-di-β-napthyl-p-phenylenediamine) at 61^{o}C was 0.84dl./g..

2. Preparative scale polymerization of decanal in MCH with LTB initiator using a controlled temperature program. A flamed out 250ml. three-necked round-bottomed flask, fitted with a paddle type stirrer and glass bushing, a Teflon thermometer adapter fitted with a short glass rod, and a ground glass joint fitted with a 3-way stopcock, served as the polymerization vessel. The apparatus was assembled hot and cooled under a blanket of dry N_2. The flask was charged with MCH (95ml.) and 6ml. of a 0.59M solution of LTB in MCH (0.004 mole LTB).

The stirrer was started and the polymerization vessel was immersed in a -20°C cold bath contained in a Dewar vessel which was equipped with an electrically controlled liquid N_2 cooling coil. After a period of 30 min. the flask was charged, with a syringe and under N_2, with decanal (16ml., 0.085 mole) and gave a clear mixture. After a period of 10 min. the bath temperature was decreased to -28°C in 5 min. and then to -35°C in 5 min.. The polymerization mixture was maintained at that temperature for 60 min. and the bath temperature was decreased to -40°C in 5 min. and maintained at that temperature for 25 min.. The bath temperature was lowered to -50°C in 10 min., held at that temperature for 10 min., then decreased to -60°C in 10 min.. After 20 min. at -60°C the bath temperature was lowered to -78°C, the Dewar vessel was packed well with CO_2(s), and the flask was left overnight at -78°C.

The stirrer was restarted and, after 1 hr., a chilled mixture of acetic anhydride (65ml., 0.60 mole) and pyridine (10ml., 0.12 mole) was added. The cold bath was gradually removed and the flask and its contents were allowed to warm to room temperature in 30 min. and agitation of the reaction mixture was continued for 1.5 hrs.. The stirrer was stopped and the reaction mixture was slowly poured into 200ml. of stirred, chilled acetone contained in a 500ml. Erlenmyer flask which was affixed in a CO_2(s)/iso-propanol bath. A fluffy white solid precipitated and 10ml. of distilled water was added to the suspension which was warmed to room temperature and filtered through a coarse fritted funnel. The solid product was washed with acetone (2x30ml.), a 1:1 mixture of acetone/water, and again with acetone. The product was then dried on the filter for 1 hr. and then transferred to a

crystallizing dish (7.1g., 51%). The product was further dried for 5 hrs. at room temperature and 0.5mm. Hg.

The infrared spectrum (pg. 259) of a film (from $CHCl_3$) of the polymer showed very strong absorptions at 2925 and 2850cm.$^{-1}$ (C-H stretch, CH_2) and moderate to strong absorptions at 1470cm.$^{-1}$ (shoulder at 1460cm.$^{-1}$, sharp shoulder at 1430cm.$^{-1}$) and 1370cm.$^{-1}$ (C-H bending, CH_2 and CH_3). A very strong, broad absorption band was recorded from 1200 to 900cm.$^{-1}$ (C-C and C-O stretching) which had notable shoulders at 1140 and 1120cm.$^{-1}$. A moderate absorption was recorded at 730cm.$^{-1}$ which had a shoulder near 740cm.$^{-1}$. A weak broad absorption, not present in the spectrum of the blank NaCl plate, was recorded in the region of 3525 to 3250cm.$^{-1}$ indicating the presence of OH endgroups or water in the sample. A weak absorption near 2725cm.$^{-1}$ indicated that the polymer was contaminated with monomeric decanal which contributed to the absorption recorded near 1720cm.$^{-1}$.

The PMR spectrum of the polymer ($CDCl_3$) (pg. 268) showed a broad absorption in the region of δ=5.05-4.65 (-O-(R)C<u>H</u>-O-) and a single strong signal at δ=1.30 ($(C\underline{H}_2)_x$). A poorly resolved multiplet, centered near δ=0.90 ($C\underline{H}_3$), was partially overlapped with the strong absorption at δ=1.30.

A small sample of the product was transferred to a test tube together with 3ml. of 2,4-dinitrophenylhydrazine reagent and the test tube was agitated in a 60^{o}C water bath. The polymer particles degraded as they became coated with yellow solid of the 2,4-dinitrophenylhydrazone.

The thick slurry of the hydrazone was filtered and the yellow

solid was washed well with ethanol, recrystallized from ethanol, and dried overnight (m.p.=103-105^{o}C, m.p. lit.[123] 104^{o}C).

The major part of the product was treated with several fresh portions of acetone for 36 hrs. at 30^{o}C. The acetone suspension was filtered and the polymer was washed with acetone and dried for 5 hrs. at room temperature and 0.1mm. Hg over KOH (75% recovery).

The inherent viscosity of a 0.51g./dl. solution of the acetone treated polymer in tetralin (contg. 0.05% N,N'-di-β-napthyl-p-phenylenediamine) at 60^{o}C was, η=1.15dl./g.. The intrinsic viscosity of the polymer in the same solvent at the same temperature was $[\eta]$=1.2dl./g..

Anal. Calcd. for $(C_{10}H_{20}O)_n$: C, 76.86%; H, 12.90%. Found: C, 76.75%; H, 12.89%.

A portion of the product polymer was reprecipitated from toluene. Polymer (1.6g.) was placed in a 250ml. Erlenmyer flask to which 200ml. of toluene was added. The flask was securely stoppered and set aside overnight at room temperature. During this time polymer seemed to have gone into solution. Distilled water (20ml.) was added to the flask and the contents of the flask were stirred for 1 hr.. The mixture was transferred to a separatory funnel and the lower aqueous layer was drawn off. The toluene layer was then added dropwise, in 1 hr., to 300ml. of virogously stirred, chilled acetone; fibrous white polymer precipitated. The suspension was allowed to warm to room temperature and then filtered through a coarse fritted funnel. The polymer coagulated to a thin, coherent, rubbery disk which was removed in one piece and cut into numerous small pieces. The reprecipitated polymer was washed with acetone and dried overnight at room temperature and

25mm. Hg.

When a sample of the product was allowed to stand for a longer period, at reduced pressure or open to the atmosphere, the sample was transformed into a yellow oil which was believed to substantially consist of monomer and was discarded.

3. Extrusion of polydecanal in a capillary rheometer. The acetone treated portion of the polydecanal, described in section I.2., was extruded at 52°C to 53°C through a tungsten carbide capillary in the capillary rheometer accessory of an Instron model TTCM. Filaments of two different diameters were extruded using capillaries of different dimensions. The first capillary had a diameter of 0.030" (0.0762cm.) and a length of 1.0078" (2.559cm.). The second capillary had a diameter of 0.050" (0.127cm.) and a length of 2.0080" (5.100cm.).

The capillary (d=0.0762cm.) was fitted to the end of the rheometer barrel and the rheometer was heated to temperature. A portion of the polymer powder was placed into the rheometer barrel and tamped with a brass rod. The plunger [0.375" (0.953cm.) dia.] was inserted and sample and plunger were allowed to preheat in the rheometer apparatus for 3.5 min.. During this period no polymer was extruded under the weight of the plunger. The crosshead was lowered, affixed to the plunger, and polymer was extruded at a crosshead speed of 0.5cm./min.. The force required to maintain the constant crosshead speed was recorded at a chart speed of 10cm./min. and a range setting which corresponded to a 100kg. load for a full scale deflection of the recorder pen.

A small, soft, nearly transparent conical shaped plug was

recovered from the barrel of the rheometer. The plug became harder, waxy and more opaque when it was cooled while soaking in acetone.

The second capillary (d=0.127cm.) was fitted to the end of the rheometer barrel and the remainder of the polymer sample was introduced through the open end of the barrel, the small plug recovered from the first extrusion was introduced last. The extrusion was then repeated with all other conditions exactly as above.

Both extrudates were cut into a number of 10-20cm. pieces and soaked in several fresh portions of acetone at room temperature for 2 hrs.. The 0.0762cm. and the 0.127cm. extrudates were stored in the freezer (-15^{o}C) under fresh acetone in tightly stoppered test tubes. The filaments were rinsed with acetone, blotted dry on filter paper, and dried at room temperature at reduced pressure prior to their use in further studies.

The bulk of the samples of both extrudates was stored in the freezer for ca. 10 days. The extrudates were cut with a razor blade to form a molding powder which was washed well with acetone and dried for 5 hrs. at room temperature and reduced pressure. The polymer was then re-extruded at 59^{o} to 60^{o}C through a tungsten carbide capillary in the capillary rheometer accessory of an Instron model TTCM.

The capillary was fitted to the end of the rheometer barrel and the rheometer was heated to temperature. The polymer was loaded into the rheometer barrel and tamped with a brass rod. The plunger [0.375" (0.953cm.)] was inserted and sample and plunger were allowed to preheat in the rheometer apparatus for 4 min.. During this time a very small amount of polymer was extruded from the capillary under the

weight of the plunger. The crosshead was lowered, fixed to the plunger, and the polymer was extruded at a crosshead speed of 0.5cm./min.. The force required to maintain the constant crosshead speed was recorded at a chart speed of 10cm./min. and a range setting corresponding to a 100kg. load for a full scale deflection of the recorder pen.

An odor of decanal was noted in the vicinity of the rheometer and the filament extrudate appeared to have a very thin coating of a liquid on its surface. The filament became more brittle and opaque as it cooled.

The extrudate was cut into a number of 10-20cm. pieces and soaked with several fresh portions of acetone at room temperature for 3 hrs.. The filament was stored in the freezer (-15^{o}C) under fresh acetone in tightly stoppered test tubes. The extrudate was washed with acetone, blotted dry on filter paper, and dried for several hours at room temperature at reduced pressure prior to its use.

4. Mechanical treatment of extruded filaments of polydecanal. The polydecanal filament, extruded at 58^{o} to 60^{o}C through a 0.030" (0.0762cm.) capillary, was used in these experiments.

a. Attempted cold drawing. Only sections of the filament which were straight and free from set curvature were used in these experiments. A hand operated stretching rig, for use in infrared studies, was employed. The jaws of the rig consisted of rectangular bars of brass stock (8x0.6x0.2cm.), closed by hex nuts on machine screws which passed through holes in the plates. Fine grit sand paper was glued to the mating faces of the jaws. The sample lengths and initial jaw separations were in the range of 3cm. to 6cm.

Although the filament samples had some flexibility they were easily crushed by a force perpendicular to their long axis. By and large the samples failed within or at the jaws before elongation of the specimen could be attempted. Shims of various thicknesses, fashioned from aluminum foil, were employed in usually futile attempts to circumvent the crushing problem and, again, the samples failed at or within the jaws.

b. Attempted cold rolling. A hand operated cold rolling device was used in these experiments. The stainless steel spring separated rolls, whose separation could be adjusted by turning two thumb screws, could be rotated in the same direction and with the same angular velocity by turning a hand crank.

When roller separations of 0.021", 0.024", or 0.026" were employed initially the samples became severely flattened and fractured into a number of long thin splinters, many of which could be easily pulled apart from each other. Many of the splinters could themselves be pulled apart into very thin splies or fibrils.

In one trial the filament was passed three times through a roll separation of 0.028". The roll separation was then decreased to 0.024" in a series of four steps. After each step decrease the filament was passed through the rolls four times. Following this treatment the filament, which was still one coherent piece, was much more opaque than the starting material and had a marbled appearance.

J. Polyundecanal [Poly((2-n-decyl)oxymethylene)]

1. Attempted preparative scale polymerization of undecanal in MCH

with LTB initiator. A flamed out 500ml. round-bottomed three-necked flask, fitted with a paddle type stirrer, a ground glass stopper fitted with a Teflon sleeve, and a ground glass joint fitted with a 3-way stopcock, served as the polymerization vessel. The apparatus was assembled not and cooled under a blanket of dry N_2.

The flask was charged with methylcyclohexane (195ml.) and 4.9ml. of a 0.612M solution of LTB in MCH (0.003 mole LTB). The stirrer was started and the flask was immersed in a cooling bath which was contained in a Dewar vessel and maintained at -60^{o}C by judicious addition of small quantities of CO_2(s) to the bath medium. After a period of 30 min. the flask was charged with distilled undecanal (13ml., 0.063 mole) and the polymerization mixture immediately became a thick slush of finely divided white particles. After a period of 3 hrs. the stirrer was stopped, the Dewar vessel was packed well with CO_2(s), and the flask and its contents were allowed to sit for 18 hrs. at -78^{o}C.

The stirrer was restarted and a chilled mixture of acetic anhydride (60ml., 0.64 mole) and pyridine (15ml., 0.19 mole) was added to the well stirred polymerization mixture. After 30 min. the cooling bath was removed in such a way that the flask and its contents warmed to room temperature in 30 min.. Mechanical stirring of the reaction mixture was continued for 30 min. and the stirrer was then stopped; the reaction mixture appeared cloudy and had only a very small amount of solid in suspension. The reaction mixture was filtered and a compact mass of a tacky solid was collected on the frit. The solid was washed with acetone (50ml.) and a 5:1 mixture of acetone and distilled water (3x35ml.). When a small volume (ca. 5ml.) of distilled water was added

near the end of the final washing the solid on the frit was dissolved away. The filtrate apparently contained no polymer and was discarded.

2. Preparative scale polymerization of undecanal in MCH with LTB initiator using a controlled temperature program. A flamed out 250ml. three-necked round-bottomed flask, fitted with a paddle type stirrer with glass bushing, a ground glass stopper with a Teflon sleeve, and a ground glass joint fitted with a 3-way stopcock, served as the polymerization vessel. The apparatus was assembled hot and cooled under a blanket of dry N_2. The flask was then charged with MCH (100ml.) and 9ml. of a 0.324M solution of LTB in MCH (0.0029 mole LTB) and the stirrer was started. The flask was then immersed in a $-17^{o}C$ cold bath contained in a Dewar vessel which was equipped with an electrically controlled liquid N_2 cooling coil.

After 30 min. the flask was charged with undecanal (20ml., 0.097 mole). After a period of 10 min. the bath temperature was lowered to $-31^{o}C$ in 1 hr. in a sequence of steps of $5^{o}C$ to $8^{o}C$ each. The bath temperature was held at each intervening temperature for approximately 5 min.. The bath temperature was maintained at $-31^{o}C$ for 15 min. and then gradually and continuously lowered to $-40^{o}C$ in 5 min.. As the bath temperature reached $-36^{o}C$ precipitation was observed in the polymerization mixture and the appearance of a slurry was accompanied by an increase in the viscosity of the mixture and formation of a number of highly swollen particles. The bath temperature was raised to $-30^{o}C$ and maintained at that temperature for 20 min.. No significant change in the visual appearance of the reaction mixture was observed. The bath temperature was brought to $-75^{o}C$ in 20 min., the stirrer was

stopped, the Dewar vessel was packed well with CO_2(s), and the flask was allowed to sit overnight at -78°C.

The stirrer was restarted and a chilled mixture of acetic anhydride (65ml., 0.60 mole) and pyridine (10ml., 0.12 mole) was added to the flask. After 15 min. the cooling bath was removed and agitation of the reaction mixture was continued for 1.5 hrs.. The stirrer was stopped and the reaction mixture was slowly poured into 400ml. of well stirred, chilled acetone contained in an Erlenmyer flask which was affixed in an ice bath. A suspension of white polymer resulted which was filtered through a 150ml. medium fritted funnel. The product was washed with acetone (4x20ml.), a 5:1 mixture of acetone/water, again with acetone, and dried on the filter for 1 hr.. The polymer was transferred to a crystallizing dish (2.5g., 15%) and dried overnight at room temperature and 25mm. Hg. For further purification the polymer sample was suspended in acetone at 30°C. After 10 hrs. the suspension was filtered and the polymer was washed with acetone then dried overnight at room temperature and 25mm. Hg.

The infrared spectrum (pg. 259) of a film of the product (from $CHCl_3$) showed very strong absorption in the region of 3050 to 2800cm.$^{-1}$ with maxima near 2925 and 2850cm.$^{-1}$ (C-H stretch). Moderate to strong absorptions were recorded at 1470cm.$^{-1}$ (shoulders at 1460 and 1430cm.$^{-1}$) and 1370cm.$^{-1}$ (shoulder near 1340cm.$^{-1}$) (C-H bending). A strong, broad absorption band was recorded from 1200 to 900cm.$^{-1}$ which had shoulders near 1120 and 1140cm.$^{-1}$ (C-C and C-O vibrations). A weak, broad absorption in the region of 3550 to 3225cm.$^{-1}$ suggested the presence of hydroxyl endgroups or water in the polymer sample. A weak absorption

near 2725cm.$^{-1}$ indicated that monomeric aldehyde present in the sample was contributing the absorption near 1720cm.$^{-1}$ ($\nu_{C=O}$).

A small sample of the product was placed in a test tube together with 3ml. of 2,4-dinitrophenylhydrazine reagent and reaction was allowed to proceed overnight at room temperature; a thick slurry of yellow solid was obtained. The slurry was filtered and the solid was recrystallized from ethanol and dried overnight at room temperature and 0.1mm. Hg (m.p.=105^{o}C, lit.[123] 104^{o}C).

The inherent viscosity of a 0.48g./dl. solution of the polymer in tetralin (contg. 0.05% N,N'-di-β-napthyl-p-phenylenediamine) was η=1.3dl./g. at 61^{o}C and η=0.51dl./g. at 80^{o}C. The intrinsic viscosity in the same solvent at 80^{o}C was [η]=0.33dl./g..

The number average molecular weight by VPO (37^{o}C in benzene) was 7,000 (DP_n-100).

Anal. Calcd. for $(C_{11}H_{22}O)_n$: C, 77.58%; H, 13.02%. Found: C, 77.31%; H, 12.91%.

3. Preparative scale polymerization of undecanal in MCH with LTB initiator employing a controlled temperature program at lower monomer concentration. A flamed out 250ml. three-necked round-bottomed flask, fitted with a paddle type stirrer and glass bushing, a Teflon thermometer adapter fitted with a glass rod, and a ground glass joint fitted with a 3-way stopcock, served as the polymerization vessel. The apparatus was assembled hot and cooled under a blanket of dry N_2. The flask was then charged with MCH (80ml.) and 4.8ml. of a 0.479M solution of LTB in MCH (0.0023 mole LTB). The stirrer was started and the flask was immersed in a -19^{o}C cooling bath contained in

a Dewar vessel which was fitted with an electrically controlled liquid N_2 cooling coil.

After 20 min. the flask was charged with undecanal (8ml., 0.039 mole). After 10 min. the bath temperature was then decreased from -19°C to -45°C over a period of 2.25 hrs. in several decrements of 2°C to 4°C each. Each decrease was accomplished in 2-3 min. and the bath temperature was maintained at each new temperature for 5-8 min. before the next decrease. The bath temperature was maintained at -45°C for 10 min. and then gradually and continuously decreased to -48°C in 10 min. and held at -48°C for 10 min.. An increase in the viscosity of the polymerization mixture was noticed. The temperature of the cooling bath was gradually decreased to -58°C in 10 min.. The polymerization mixture had become a stiff slurry.

The bath temperature was then gradually decreased to -60°C in 10 min.. The bath temperature was brought to -78°C, the stirrer was stopped, the Dewar vessel was packed well with CO_2(s), and the flask and its contents were allowed to sit overnight at -78°C.

The stirrer was restarted and, after a period of 30 min., a chilled mixture of acetic anhydride (70ml., 0.74 mole) and pyridine (10ml., 0.12 mole) was added to the mixture. After a period of 15 min. the cold bath was removed and the flask was warmed to room temperature in 45 min. and agitation of the reaction mixture was continued for 1 hr.. The stirrer was stopped, and the reaction mixture was slowly poured into 300ml. of well stirred chilled acetone contained in a 1 l. Erlenmyer flask which was affixed in an ice bath. The polymer precipitated and the suspension of polymer was suction filtered through a

150ml. medium fritted funnel and the tacky caky product was washed with acetone (4x30ml.). The product was transferred to a 125ml. Erlenmyer flask and suspended in a mixture of acetone (75ml.) and distilled water (15ml.) with vigorous stirring. After being stirred at room temperature for 30 min. the suspension was filtered and the solid was washed with acetone then dried overnight at room temperature and 25mm. Hg (yield 3.1g., 46%).

The infrared spectrum (pg. 260) of a film (from $CHCl_3$) of the polymer showed strong absorptions at 2925cm.$^{-1}$ (shoulder near 2975cm.$^{-1}$) and 2850cm.$^{-1}$ (shoulder near 2875cm.$^{-1}$) (C-H stretching). A moderate to strong absorption was recorded at 1470cm.$^{-1}$ (shoulders at 1460 and 1440cm.$^{-1}$) as was a moderate absorption near 1380cm.$^{-1}$, which may have been split into a doublet (C-H bending). Absorptions near 1140 and 1120cm.$^{-1}$ were recorded as pronounced shoulders on the generally broad absorption band in the region of 1200 to 900cm.$^{-1}$ which had maximum absorption near 1100cm.$^{-1}$.

The inherent viscosity of a 0.51g./dl. solution of the polymer in tetralin (contg. 0.05% N,N'-di-β-napthyl-p-phenylenediamine) at 60^{o}C was η=0.82dl./g..

The number average molecular weight by VPO (37^{o}C in benzene) was ca. 15,000 (DP_n=85).

Anal. Calcd. for $(C_{11}H_{22}O)_n$: C, 77.58%; H, 13.02%. Found: C, 77.54%; H, 13.01%.

4. Extrusion of polyundecanal in a capillary rheometer. Polyundecanal was extruded through a tungsten carbide capillary at a temperature of 59^{o} to 60^{o}C in the capillary rheometer accessory of an

Instron model TTCM. The diameter of the capillary was 0.030" (0.762cm.) and its length was 1.0078" (2.559cm.).

The capillary was fitted to the end of the rheometer barrel and the rheometer was heated to temperature. The polymer powder was introduced into the rheometer barrel and tamped with a brass rod. The plunger (0.375" (0.953cm.) dia.) was inserted and sample and plunger were allowed to preheat for 3 min.. During this time a very small amount of material was extruded under the weight of the plunger. The crosshead was lowered, affixed to the plunger, and the polymer was extruded at a crosshead speed of 0.5cm./min.. The force required to maintain the constant crosshead speed was recorded at a chart speed of 10cm./min. and a range setting corresponding to a full scale deflection of the recorder at a load of 100kg.. A smooth regular force trace was recorded. An odor of undecanal monomer was noted in the vicinity of the rheometer during the extrusion. The filament extrudate appeared very uniform with only very small bubbles or other irregularities near the center of the extrudate.

The filament was cut into a number of 10-20cm. pieces which were soaked with several fresh portions of acetone at room temperature for 2 hrs.. The extrudate was stored in the freezer under fresh acetone in a tightly stoppered test tube. The filament pieces were rinsed with acetone, blotted dry with filter paper, and dried in vacuo for several hours at room temperature prior to their use.

K. Polydodecanal [Poly((2-n-undecyl)oxymethylene)]

1. Exploratory scale polymerization of dodecanal in toluene

with LTB initiator. Four tared 50ml. round-bottomed microglass flasks, closed with serum stoppers, were charged, via syringe and under N_2, with a volume of dodecanal (distilled once). The flasks were weighed to determine the weight of the aldehyde and then charged with toluene. The weights of dodecanal and the volumes of toluene are given in the schedule below. Each flask was then cooled and charged with a 0.30M solution of LTB in MCH.

	A	B	C	D
g. aldehyde	2.7	4.1	9.0	4.2
mole aldehyde	0.015	0.022	0.049	0.023
ml. toluene	13	26	33	13
ml. 0.30M initiator solution	0.9	1.5	3.0	1.5
mole% initiator	2	2	2	2

None of the mixtures was a one phase system at temperatures below ca. -25°C. Depending upon temperature and relative concentrations of reagents the contents of the various vessels appeared as a thick blue-white gelatinous sludge or as a stiff slush of white particles.

Three different cooling baths, maintained at different temperatures, were used at various times in the course of the experiment. One bath was maintained at -20°C (ice/salt), a second bath was maintained at -45°C to -50°C (70;30, w:w, glycerine:water; cooled with CO_2(s)), and a third bath was maintained at -78°C (CO_2(s)/iso-propanol). Whenever a flask was charged with a reagent or transferred to a bath which was maintained at a lower temperature than the one from which it was taken a syringe needle, connected via a glass tee to a source of dry

N_2 and a Hg filled checkvalve, was inserted through the serum stopper closure of the flask. The needle was removed after the manipulation.

Flask A, charged with the indicated amount of solvent and initiator, was cooled in a bath maintained at -20°C for a period of 20 min., and the indicated volume of aldehyde was added; the flask and its contents were then agitated and allowed to remain in the -20°C bath for 20 min.. The flask was removed from the -20°C bath and placed in a bath maintained at -45°C where it was allowed to remain for 30 min.. The flask was swirled by hand for a period of 10 min. while being immersed in a bath maintained at -78°C. The contents of the flask, which constituted a clear one phase system at -20°C, became viscous and developed a bluish opalescence when cooled to -45°C and transformed into a solid blue-white plug when cooled to -78°C. The flask and its contents were allowed to sit at -78°C for 18 hrs..

Flask B was treated in an identical manner, excepting that the period of reaction at -45°C was omitted.

A volume (1ml.) of a 4.5M solution of acetic anhydride in pyridine was charged into tube A and a volume of trimethyl orthoformate (0.2ml.) was charged into tube B. Both flasks were then agitated by hand and placed in a bath maintained at -45°C where they were allowed to remain for a period of 1 hr.. Flask B broke and its contents spilled into the low temperature bath, tube A was transferred to a bath maintained at -20°C. After 30 min. the viscous, slightly cloudy contents of the flask were poured into a well chilled (0°C), magnetically stirred volume (50ml.) of a 1:4 mixture of dimethylformamide and methanol. The suspension was suction filtered through a coarse fritted funnel. The

tacky granular solid was washed with several portions of the dimethyl-formamide-methanol mixture. The product was dried on the filter for 1 hr., then dried overnight at room temperature and reduced pressure (20mm. Hg) (0.9g., 33%).

Tubes C and D were charged with the indicated amounts of aldehyde and solvent and then placed in a bath maintained at -20°C. After 20 min. each flask was then charged with initiator solution, agitated, and allowed to remain at -20°C for 30 min.. The flasks were shaken by hand for 10 min., and immersed for increasing intervals of time in a bath maintained at -78°C.

After 36 hrs. at -78°C flasks C and D were then transferred to a bath maintained at -20°C. After 10 min. the contents of flask D were clear while the contents of tube C were a slightly viscous liquid. Both flasks were then placed in a bath maintained at -45°C for 30 min. and then transferred to a bath maintained at -78°C where they were kept for 1 hr..

One ml. of a 4.5M solution of acetic anhydride in pyridine was charged into flask C which was then transferred to a bath maintained at -20°C where it was kept for a period of 1.5 hrs.. Acetyl chloride (0.2ml.) was charged into flask D which was then transferred to a -45°C bath. After 30 min. flask D was transferred to a -20°C bath and kept for 1 hr.. The contents of each of tubes C and D were poured into separate magnetically stirred, chilled (0°C) volumes (50ml.) of a 1:4 (v:v) mixture of dimethylformamide and methanol. The suspensions were suction filtered through separate coarse fritted funnels and the collected solids were washed with several portions of the dimethyl-

formamide-methanol mixture, dried on the filter for 1 hr., then dried overnight at room temperature and reduced pressure (20mm. Hg). The yield from flask C was 1.2g., 21%, only a trace amount of product was obtained from the reaction mixture of flask D. Before the sample was dried for characterization a portion of the solid obtained from the reaction mixture of tube C was ground with several fresh small portions of methanol and dried.

The methanol treated portions of samples A and C were soluble in $CDCl_3$, but the solutions did not show an appreciable viscosity. The PMR spectra of the two samples (pg. 269, 270) were quite similar and agreed with the -O-CH(R)-O-CH(R)- structure of the product.

A portion of the methanol washed sample obtained from the reaction mixture of flask A was dissolved in $CHCl_3$. The solution was spread onto a NaCl plate and allowed to evaporate which gave a very poor film, the infrared spectrum of which was recorded (pg. 260). The spectrum was dominated by absorptions assignable to deformations of C-H bonds. Strong absorptions were also observed near 1120cm.$^{-1}$ and 1160cm.$^{-1}$ which were attributed to skeletal C-O-C vibrations.

Anal. Calcd. for $(C_{12}H_{24}O)_n$: C, 78.20%; H, 13.12%. Found: (product A), C, 78.76%; H, 12.80%; (product C), C, 78.82%; H, 12.91%.

A sample of the product obtained from flask A was degraded with acidic 2,4-dinitrophenylhydrazine reagent. It was necessary to heat the reaction to 60^{o}C for several minutes and then to allow the reaction to proceed overnight to form the 2,4-dinitrophenylhydrazone which was obtained as thick slurry which was turned out onto a fritted funnel, with suction, and the collected solid was washed with

several portions of warm (60°C) glacial acetic acid followed by several portions of methanol. The derivative was dried on the filter for 1 hr., then dried overnight at reduced pressure (20mm. Hg) (m.p.=104-106°C, m.p. lit.[123]=107°C).

When treated similarly, the sample obtained from the reaction mixture of flask B behaved similarly, and it was found that the degradation could be facilitated by addition of a small amount of conc. H_2SO_4 before introduction of the derivatizing reagent (m.p.=104-106°C, m.p. lit.[123]=107°C).

2. Attempted preparative scale polymerization of dodecanal in MCH with LTB initiator using a controlled temperature program. A flamed out 250ml. three-necked round-bottomed flask fitted with a paddle type stirrer with glass bushing, a Teflon thermometer adapter fitted with a short length of glass rod, and a ground glass joint fitted with a 3-way stopcock, served as the polymerization vessel. The apparatus was treated as described in section D.1..

The flask was charged, via syringe and under N_2, with MCH (100ml.) and 5.3ml. of a 0.63M solution of LTB in MCH. The stirrer was started and the polymerization vessel was immersed in a -20°C cooling bath contained in a Dewar vessel which was fitted with an electrically controlled liquid N_2 cooling coil. After a period of 30 min. the flask was charged with twice distilled dodecanal (11ml., 0.049 mole). After 15 min. the temperature of the bath was brought to -27°C over a period of 1 hr. in a series of decrements of 2-3°C each. Each temperature decrease was accomplished in a 5 min. period and the bath temperature was maintained at each intervening temperature for 15 min.. As the

bath temperature was decreased to -27°C the polymerization mixture appeared to thicken slightly and an indication of a precipitate was observed. The bath temperature was maintained at -27°C for 15 min. during which time the precipitate appeared to intensify and the polymerization mixture became cloudy.

The bath temperature was then brought to -60°C over a period of 2 hrs. in a series of decrements of 3-5°C each. Each temperature decrease was accomplished over a 5 min. period and the bath temperature was maintained at each intervening temperature for 15 min. before the next temperature decrease. The relative amount of precipitate continued to increase and the appearance of the precipitate ranged from hard blue-white globules (1-2mm. nominal dimensions) to granular white solid.

The bath temperature was maintained at -60°C for 15 min. and then decreased to -78°C. The reaction mixture appeared as a very thick slush of fine white solid. The stirrer was stopped, the dewar vessel was packed well with CO_2(s), and the flask and its contents were allowed to sit overnight at -78°C.

The stirrer was restarted and, while a strong stream of N_2 was passed through the three way stopcock, the thermometer adapter was momentarily raised and a well chilled mixture of acetic anhydride (75ml., 0.79 mole) and pyridine (25ml., 0.31 mole) was poured into the flask containing the essentially solid slush of the polymerization mixture. After a period of 15 min. the cold bath was removed and the flask and its contents were allowed to warm to room temperature in 40 min.. If the stirrer was momentarily stopped after the reaction mixture had warmed to room temperature the reaction mixture appeared

to segregate into two phases, a clear yellowish upper layer and a cloudy blue white lower layer. Mechanical agitation of the room temperature reaction mixture was continued for 75 min..

The stirrer was stopped and the reaction mixture was slowly poured into 450ml. of chilled ($0^{o}C$) acetone contained in a 1 l. Erlenmyer flask which was affixed in an ice bath. A very small amount of very highly swollen precipitate could be observed in the turbid mixture which was suction filtered through a medium fritted funnel. The filtration proceeded very slowly.

When the filtration was complete the very thin cake of pasty off-white solid which had deposited on the frit was suspended in 20ml. of acetone with the aid of a glass rod. The acetone washing was drawn off through the frit with suction and the procedure was repeated 4 times. When a small volume (ca. 2ml.) of distilled water was added to the last portion of acetone, the suspended solid dissolved completely. No characterization of the combined filtrates, which reeked of dodecanal, was attempted.

3. Attempted preparative scale polymerization of dodecanal in toluene with LTB initiator using a controlled temperature program. A flamed out 250ml. three-necked round-bottomed flask fitted with a paddle type stirrer with glass bushing, a Teflon thermometer adapter fitted with a short length of glass rod, and a ground glass joint fitted with a three way stopcock served as the polymerization vessel. The apparatus was treated as described in section D.1..

The flask was charged, via syringe and under N_2, with toluene (100ml.) and 8.0ml. of a 0.37M solution of LTB in MCH (0.0029 mole LTB).

The stirrer was started and the vessel was immersed in a -20°C bath contained in a Dewar vessel which was equipped with an electrically controlled liquid N_2 cooling coil. After a period of 20 min. the flask was charged, via syringe and under N_2, with twice distilled dodecanal (8.5ml., 0.038 mole).

After 10 min. the bath temperature was lowered from -20°C to -45°C in 3.5 hrs. in numerous decrements of 2-3°C each. Each decrease was accomplished in 2 to 3 min. and the bath temperature was maintained at the new temperature for 5 to 8 min. before the next decrease.

The bath temperature was held at -45°C for 5 min. and then gradually brought to -48°C in 2 min. and the bath was maintained at that temperature for a period of 15 min.. During this period, a slight change in the appearance of the polymerization mixture was observed. The viscosity of the mixture had increased and the transparency of the mixture had decreased slightly.

The temperature of the bath was then gradually lowered from -48°C to -51°C in 5 min. and then maintained at -51°C for 15 min.. The bath temperature was then gradually and continuously lowered to -57°C over a period of 20 min.. During this interval marked changes were observed in the appearance and behavior of the polymerization mixture. A band of thick, glassy material, approximately 5mm. wide and possessing a pale blue-white tint, was observed on the interior surface of the polymerization vessel, just above the level of the bulk of the polymerization mixture. The bulk of the polymerization mixture appeared viscous and possessed a pale blue tint. The bath temperature was maintained at -57°C for 20 min..

The bath temperature was gradually and continuously lowered, over a period of 15 min., to -64°C, maintained at -64°C for 15 min., and then decreased to -75°C in 15 min.. The stirrer was stopped, the Dewar vessel was packed well with CO_2(s), and the flask and its contents were allowed to sit in the cold bath overnight.

The stirrer was restarted, the thermometer adapter was momentarily raised, and a well chilled mixture of acetic anhydride (65ml., 0.69 mole) and pyridine (10ml., 0.12 mole) was poured into the flask while a strong stream of N_2 was maintained over the polymerization mixture via the 3-way stopcock. A partial clearing of the polymerization mixture was observed. After a period of 15 min. the reaction mixture appeared much whiter.

The cold bath was removed in such a way that the flask and its contents warmed to room temperature over a period of 1 hr.. Mechanical agitation of the reaction mixture was continued for 1 hr.. The stirrer was stopped and the reaction mixture was slowly poured into a magnetically stirred volume (300ml.) of chilled (0°C) acetone contained in a 1 l. Erlenmyer flask which was affixed in an ice bath. A small amount of bluish white precipitate was observed.

The mixture was suction filtered and a very small amount of a white slush/paste was collected on the frit. The material on the frit was washed with several small portions of acetone and dried on the filter for 1 hr.. During this period most of the collected solid disappeared leaving only a trace amount of off-white solid which was not further characterized. Dodecanal sodium bisulfite addition compound was isolated in near quantitative yield from the filtrate by

pouring the filtrate into a magnetically stirred volume of bisulfite reagent, prepared in the usual way[124].

The experiment was repeated with a lower initial monomer concentration (5.0g. aldehyde/100ml. solvent) following a very similar temperature profile. Instead of introducing the typical end capping reagent a volume of well chilled acetone was poured into the cold (-78°C), well stirred polymerization mixture. A suspension of very fine particles resulted which was warmed to 0°C and suction filtered through a medium fritted funnel and washed with several portions of acetone. A thin layer of jelly-like material was collected on the frit which, when washed with acetone and dried on the filter, reduced to a trace of off white caky powder.

When the filtrate was added to a volume of sodium bisulfite reagent as above, 6.1g. of a fluffy white solid was obtained (dec. 220°C).

CHAPTER III

RESULTS AND DISCUSSION

A. Aliphatic Aldehyde Monomers

1. Introduction. Aliphatic aldehydes, as a class, are known to be very reactive compounds. For this reason aliphatic aldehydes for use in polymerization and other experiments were difficult to purify and retain in a pure condition. From the point of view of the anionic polymerization of aliphatic aldehydes the impurities of primary concern were carbocylic acid, formed by oxidation of the aldehyde, and water, introduced from extraneous sources or by aldol condensation of the aldehyde followed by elimination of water from the adduct. Consideration was given to the likely presence of both contaminants in purification of the aliphatic aldehydes. In certain circumstances, particularly in the purification of hexanal, the problem of contamination of the aldehyde with water was compounded by the ability of the aldehyde to form a binary azeotrope with water. However, by the proper combination of drying agents and distillation, it was possible to obtain higher aliphatic aldehydes of sufficient purity for use in anionic polymerization experiments.

The melting behavior of certain higher aliphatic aldehydes was investigated by DSC. It was found that the melting points of nonanal, decanal, undecanal, and dodecanal are near or below room temperature if the aldehydes were purified exactly as for use in polymerization experiments. The melting behavior of the aliphatic aldehydes was investigated for two reasons. Firstly, a number of discrepancies in melting

points reported for several of the higher aliphatic aldehydes may be found in the literature and it was desired to compare the melting points of aliphatic aldehydes used in polymerization experiments, as determined by a standard technique, with the melting points reported in the literature. Secondly, it was thought likely that monomeric aldehyde might be present or formed (by degradation) in samples of higher aliphatic polyaldehydes during DSC investigation of the polymers. It was hoped that DSC investigation of the monomers, under conditions analogous to those typically employed in characterization of the polymers, might be of assistance in interpreting the DSC thermograms of the polymers.

2. Investigation of the melting behavior of aliphatic aldehydes by DSC. The higher aliphatic aldehydes used in DSC experiments had a level of purity, according to GC, comparable to that of the monomers used in more carefully controlled polymerization experiments. Volatile sample pans fabricated of gold, rather than aluminum, were used in these investigations since it had been observed that a pronounced darkening of the bottom of aluminum sample pans occurred when polyaldehyde thermal degradation products (primarily aliphatic aldehyde) were allowed to accumulate in the aluminum sample pans at elevated temperatures.

The results of DSC investigation of the melting behavior of nonanal, decanal, undecanal are summarized in Table 3. The data indicated that the melting points of those aliphatic aldehydes investigated lay near or below room temperature. In all cases the enthalpies of fusion equalled the enthalpies of crystallization within the limits of experimental error. In all cases only one endothermic transition was

TABLE 3

Melting Points and Heats of Fusion of Higher Aliphatic Aldehydes by DSC[a]

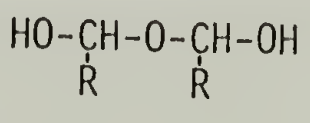
Aldehyde	Peak Temperature (in ^{o}C)	ΔH_f (±3%) (in cal./g.)	(in cal./mole)
Nonanal	-17	61.3	8,720
Decanal	-3 (-5)[b]	63.8	9,970
Undecanal	+2 (-4)[b]	66.1	11,260
Dodecanal	+13 (11, 43)[b]	68.5	12,630
Avg. increase per $-CH_2$	--	2.4	1,300

[a]At 20°C/min.. At 10°C/min. the peak temperatures were 1°C lower and heats of fusion were 6% higher.

[b]Literature data, ref.

recorded in DSC scans in the region of -75^{o} to $+100^{o}C$. In some DSC scans of undecanal and dodecanal a small shoulder was recorded on the high temperature side of the fusion endotherm. Further experiments indicated that these shoulders (restricted to endotherms recorded for larger samples at higher heating rate) were experimental artifact and not due to the occurrence of two distinct types of transitions separated by a small temperature difference.

In a number of instances the melting points of several higher aliphatic aldehydes have been reported to be above room temperature. This apparent discrepancy can be exemplified by the case of dodecanal which many years ago[130] was reported to have a melting point of $44.5^{o}C$. Klass and coworkers[58] addressed themselves to the nature of the various species, all claimed by various authors to be dodecanal, which had reported melting points which disagreed by as much as $40^{o}C$ ($12^{o}C$; $45^{o}C$). On the basis of infrared spectroscopy and chemical elemental analysis, these workers concluded that purified, free dodecanal had a melting point of $12^{o}C$ and that the melting point between $41^{o}C$ and $45^{o}C$ was most likely an aldehyde "hemihydrate" formed by the reaction of 2 mole quantities of aldehyde with one mole quantity of water, Equation 7.



Eqn. 7

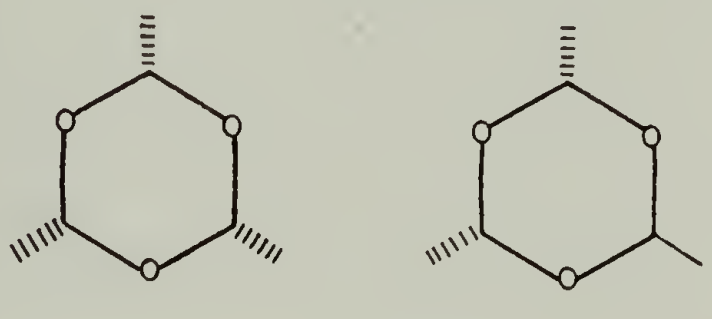
B. Aldehyde Cyclic Trimers

1. Introduction. Cyclic trimers of aliphatic aldehydes from C_9 to C_{12} whose linear polymers are reported for the first time in this

thesis, were prepared and characterized in order to compare their melting points and melting behavior with those of the corresponding polymers.

The aldehyde cyclic trimers can exist as one of two possible geometric isomers depending upon the disposition of the substituent alkyl groups with respect to each other as shown in Figure 3.

Figure 3: Possible Geometric Isomers of Aldehyde Cyclic Trimers



The all cis isomer is generally considered to be the more stable isomer on the grounds of minimum steric interaction of 1,3 substituents. The possibility of coexistence of both isomers in samples of the cyclic trimers prepared is discussed in more detail later.

Lewis acids as catalysts, particularly $SbCl_5$, in diethyl ether-pentane gave the most satisfactory results for the synthesis of the trimers. Diethyl ether or pentane alone was found to be unsuitable because of the difficulty in isolating crystalline product from the reaction mixture. Syntheses of the aldehyde cyclic trimers with $SbCl_5$ catalyst in this mixed solvent is described in Chapter II. Because of difficulties encountered in product work up, protic acids were less suitable as trimerization catalysts. The trimerization of nonanal in bulk with H_2SO_4 catalyst, described below, is simpler.

2. Nonanal cyclic trimer. Two procedures were successfully

employed for the preparation of the cyclic trimer of nonanal. In diethyl ether-pentane with $SbCl_5$ catalyst the trimer was obtained in 22% yield. In bulk with H_2SO_4 catalyst the trimer was obtained in 57% yield. The trimer did not precipitate directly in either reaction and, in both cases, an additional step was required to isolate crude product.

The trimerization of nonanal with $SbCl_5$ catalyst in diethyl ether-pentane was not as effective as in the case of other aldehyde trimerizations. Several improvements had been made but without success. Only viscous oils, rather than a crystalline solid, was ever obtained. (The monomer employed was not distilled but was simply treated with Na_2CO_3 and CaH_2). The infrared and PMR spectra of these oils indicated that they were substantially composed of nonanal cyclic trimer although the presence of unreacted aldehyde was detected. After the reaction was complete the catalyst was neutralized with NaOH, the solvent was carefully evaporated, and nonanal cyclic trimer was isolated from the resulting concentrated reaction mixture by the addition of methanol and cooling of the resulting mixture. The product was easily recrystallized from a diethyl ether-ethanol solvent mixture. The trimer of nonanal was difficult to isolate in comparison to the products from the trimerization of other higher aliphatic aldehydes which were easier to work up.

The infrared spectrum of the product (pg. 255) was consistent with the 2,4,6-tri-n-alkyl-1,3,5-trioxane structure of product.

Because the desired product could be satisfactorily prepared by a different procedure, the $SbCl_5$ catalysed trimerization of nonanal was

not further investigated.

Nonanal cyclic trimer was also prepared by the reaction of nonanal, in bulk, with H_2SO_4 catalyst. The exothermic reaction which occurred when the catalyst was added to the aldehyde gradually subsided. The product was isolated in 57% yield by pouring the reaction mixture into a mixture of diethyl ether and ethanol, cooling the resulting solution, and filtration of the resulting suspension. This straight forward procedure was only successful if the aldehyde was properly pretreated and distilled at least once before use.

When crystallized in a thin layer, either from solution or from the melt, the trimer showed a very strong tendency to crystallize in a circularly symmetric array. Depending upon the crystallization conditions either radiating bundled axialite or spherulitic morphologies were observed. The sample of nonanal cyclic trimer prepared with H_2SO_4 catalyst was used in the characterization experiments discussed below.

The infrared spectrum (KBr) (pg. 255) and the PMR spectrum ($CDCl_3$) (pg. 262) were consistent with the 2,4,6-tri-n-alkyl-1,3,5-trioxane structure of the product. The infrared spectrum was dominated by bands assignable to fundamental deformations of C-H bonds of the alkyl groups, absorptions near 1160cm.$^{-1}$ and 1120cm.$^{-1}$, in the general C-C and C-O skeletal vibration region, were assigned to C-O bond stretching in the cyclic acetal structure. The infrared spectrum of a $CHCl_3$ solution of the trimer is shown in Figure 4 (A). The PMR spectrum was dominated by absorptions of protons of the long alkyl group of the product. The triplet near δ=4.80 was assigned to the resonance of the acetalic protons of the trimer ($R\text{-}CH_2\text{-}\underline{C}H\underline{O}\text{-}$). The other absorptions in

the spectrum could be assigned to resonance absorptions of the remaining protons of the alkyl group. The PMR (90 MHz) spectrum of the trimer (in $CDCl_3$) is shown in Figure 5 (A). In the CMR spectrum seven distinct absorptions were recorded and were tentatively assigned as indicated in Figure 7 (A) (pg. 142).

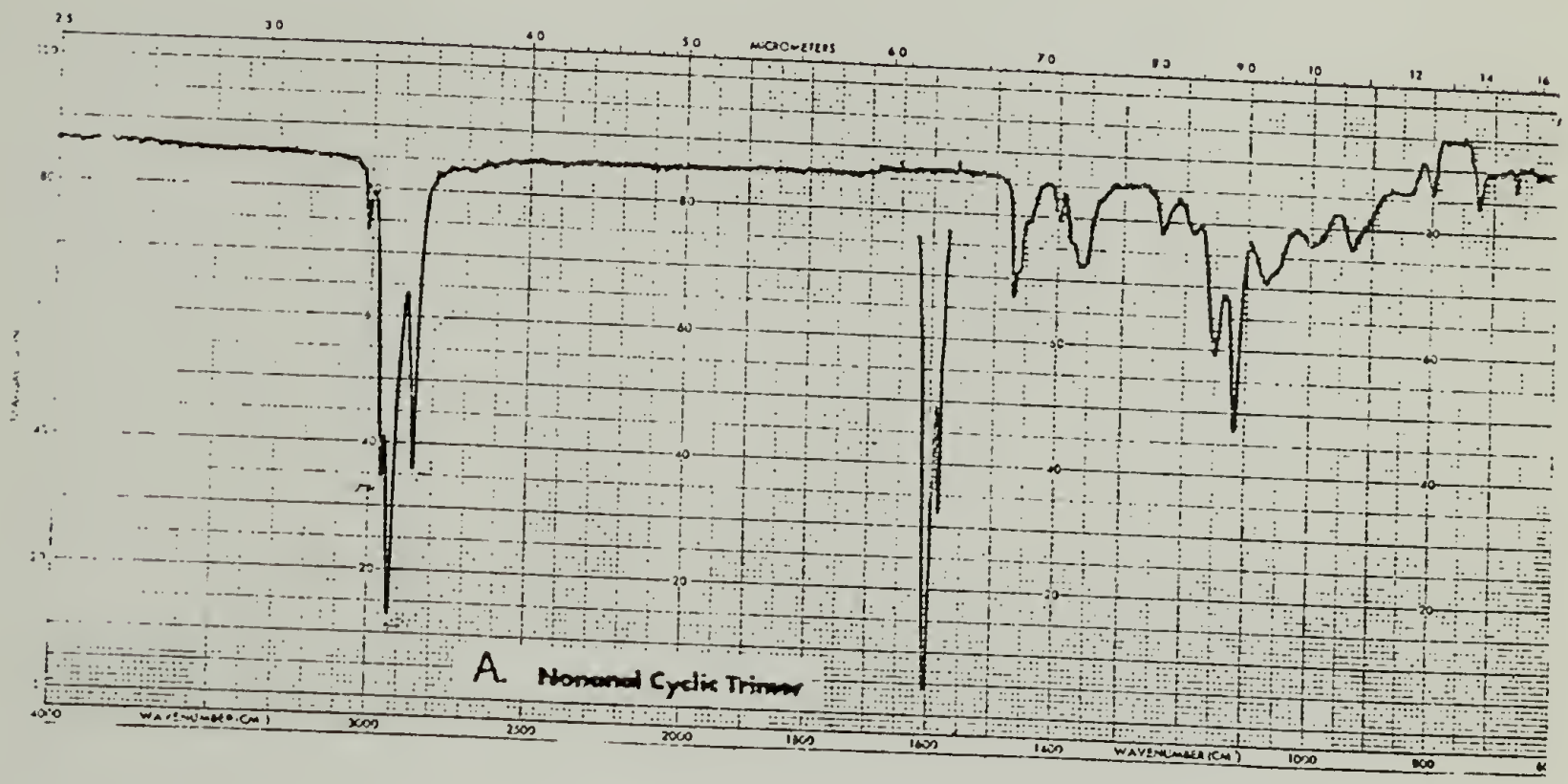
The thermal decomposition of nonanal cyclic trimer in N_2 was investigated by TGA; the results are given in Table 4 (pg. 134). The temperature of maximum rate of weight loss was similar to that observed for trimers of other higher aliphatic aldehydes. The melting behavior of the cyclic trimer was investigated by DSC under a wide variety of conditions. Results of representative runs are given in Table 5 (pg. 135). All annealing and quenching of samples was performed in the calorimeter; a significant influence of thermal history upon peak temperature and transition enthalpy was never observed. Only one endothermic transition was observed in samples between -50^{o} and $+100^{o}C$. In all cases the enthalpy associated with fusion endotherms equalled the enthalpy associated with crystallization exotherms within the limits of experimental error.

3. Decanal cyclic trimer. Decanal cyclic trimer was prepared in 95% yield from pretreated and distilled decanal when the reaction was conducted in diethyl ether-pentane with $SbCl_5$ catalyst. The product precipitated during the reaction and was readily isolated. Reaction of the aldehyde in bulk with H_2SO_4 catalyst was much less successful, regardless of the purity of the aldehyde. The product could be easily recrystallized from a diethyl ether-ethanol mixture.

The infrared spectrum (KBr) (pg. 255) and the PMR spectrum

Figure 4:

I.R. Spectra of Aldehyde Cyclic Trimers in $CHCl_3$ Solution



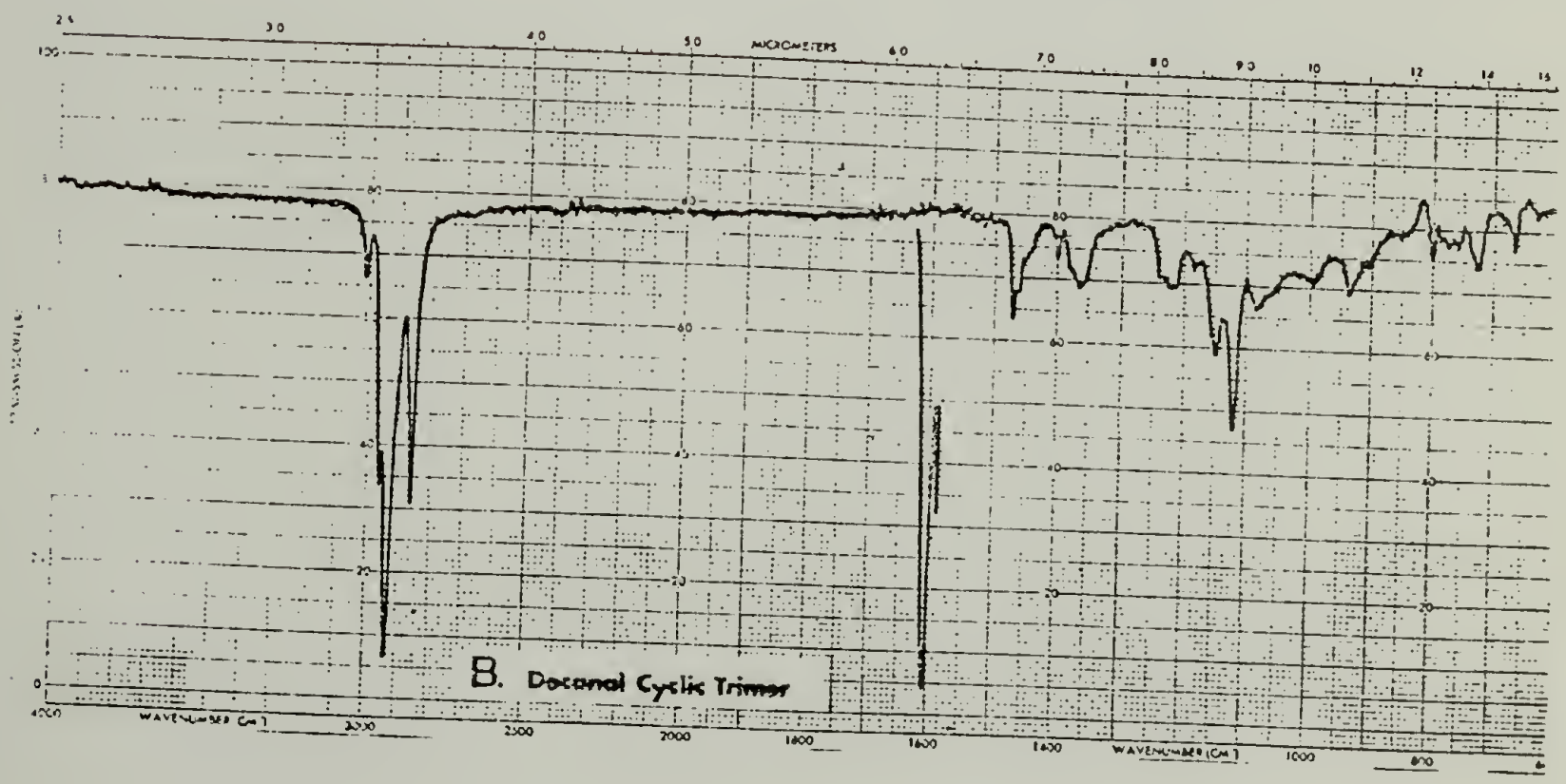
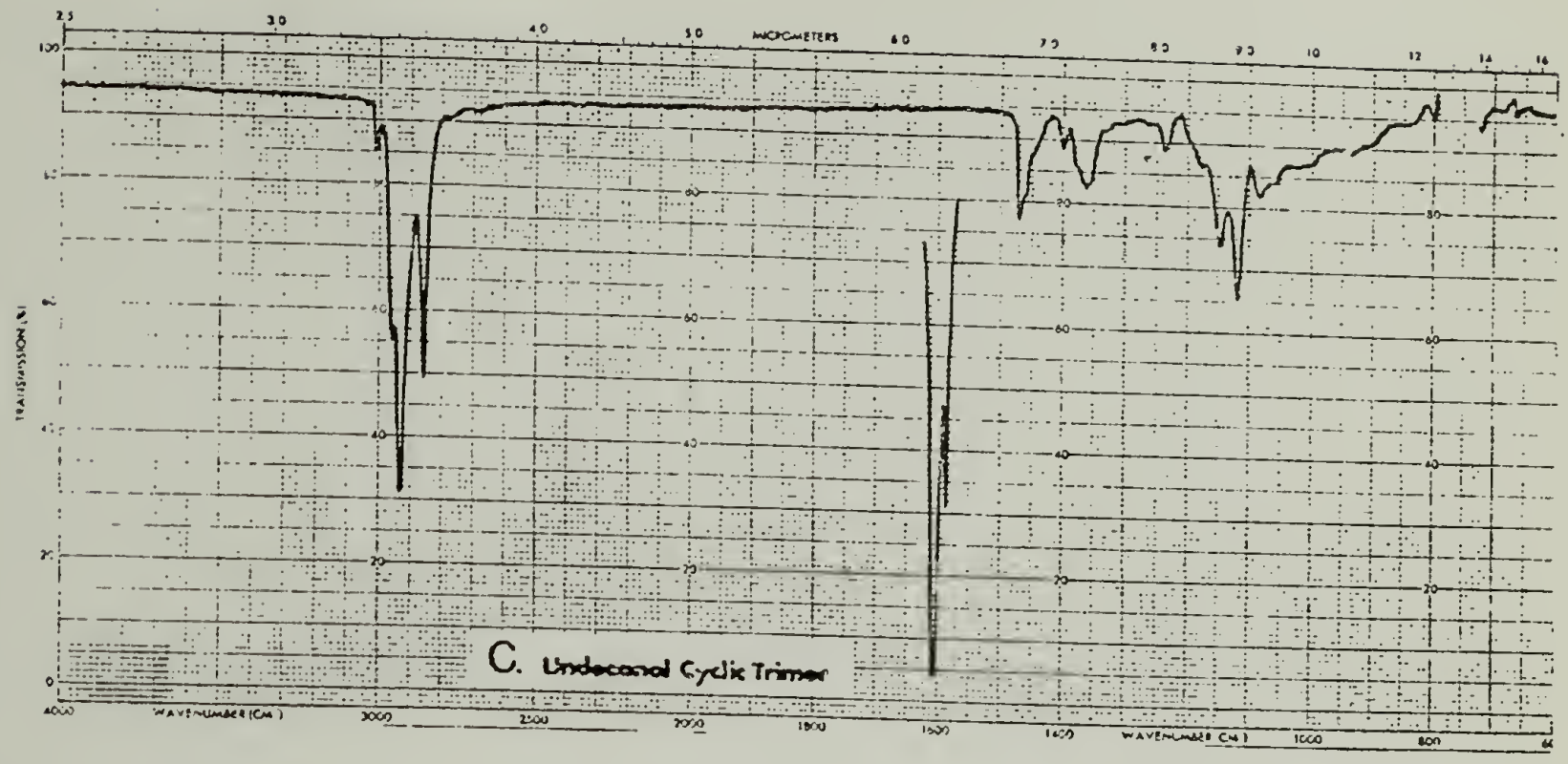


Figure 4 (cont'd):



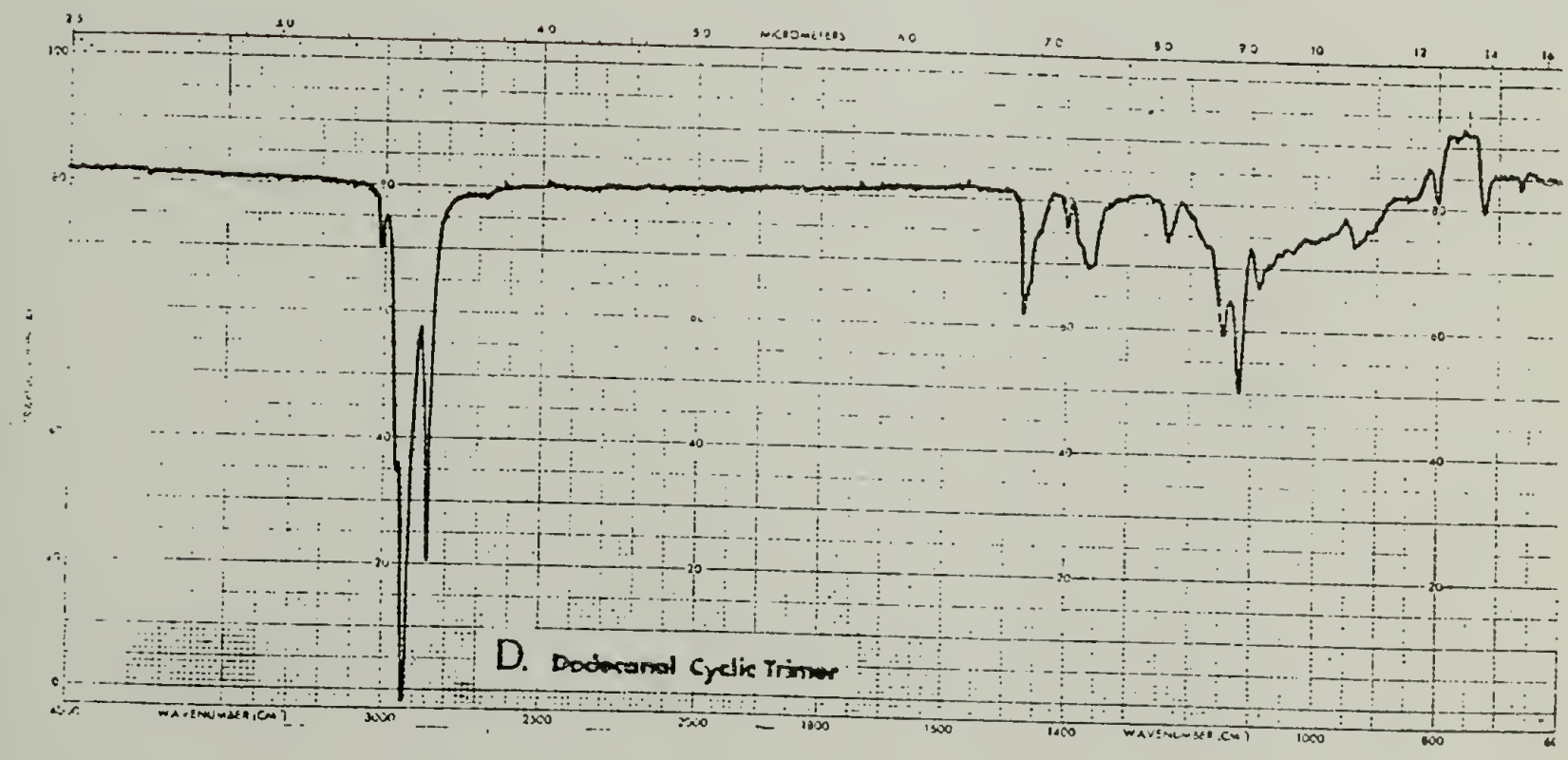
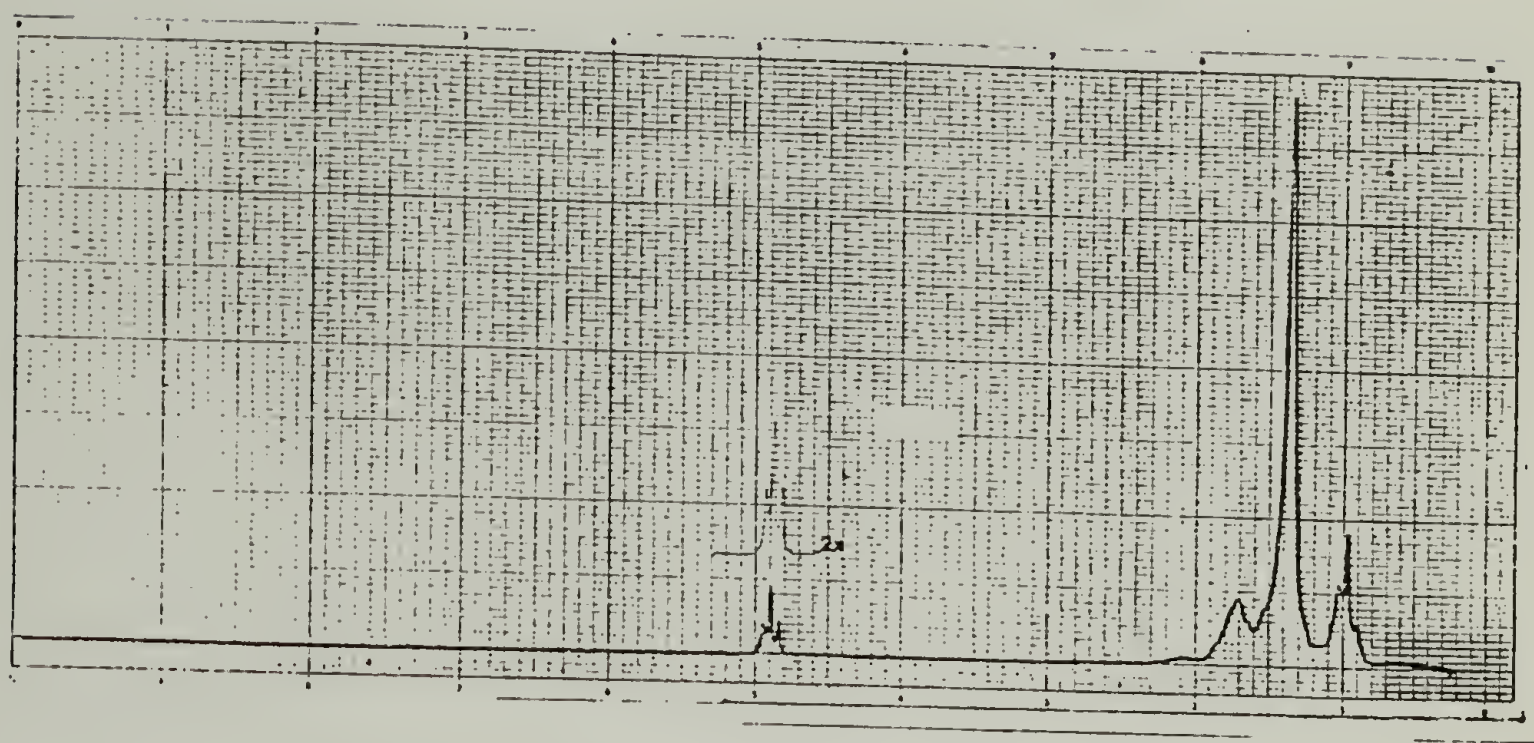
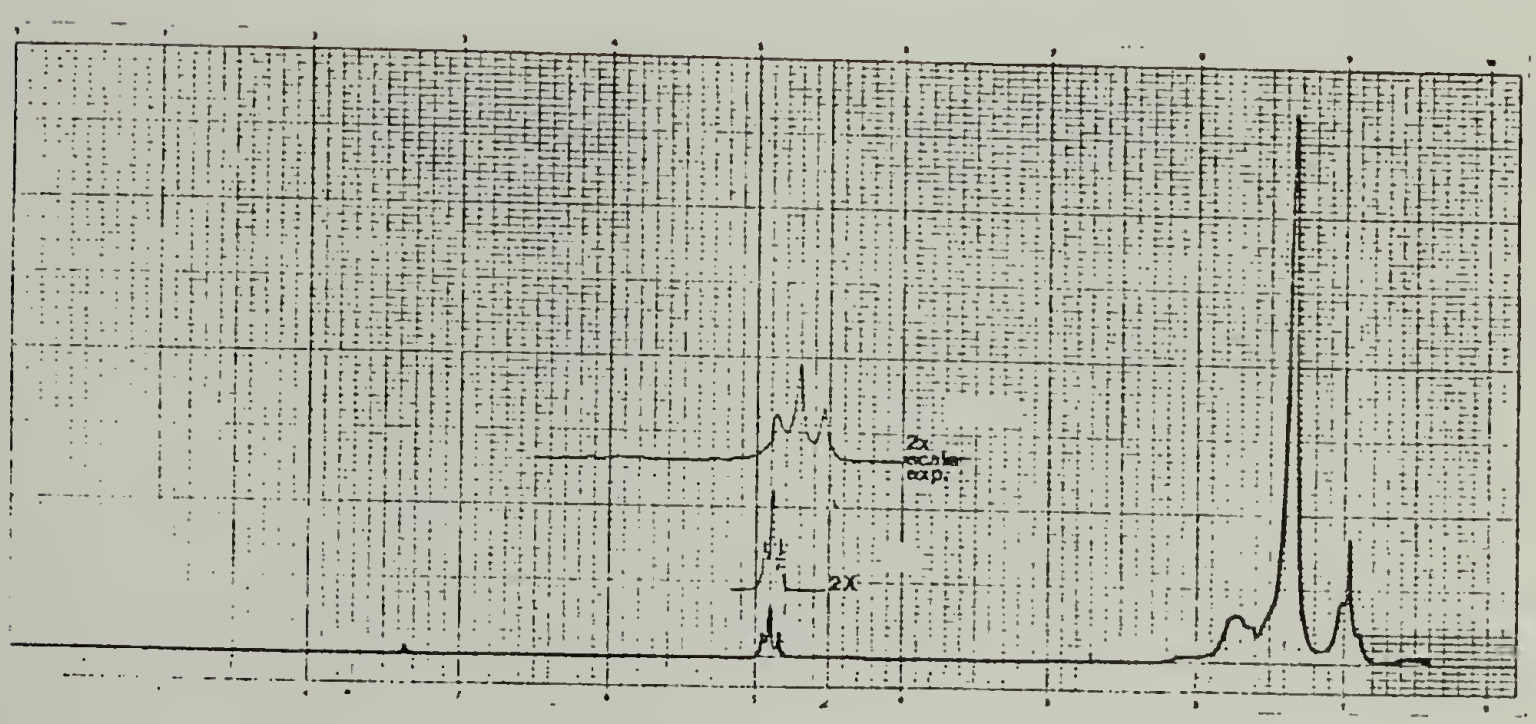


Figure 5:

90 MHz PMR Spectra of Aldehyde Cyclic Trimers

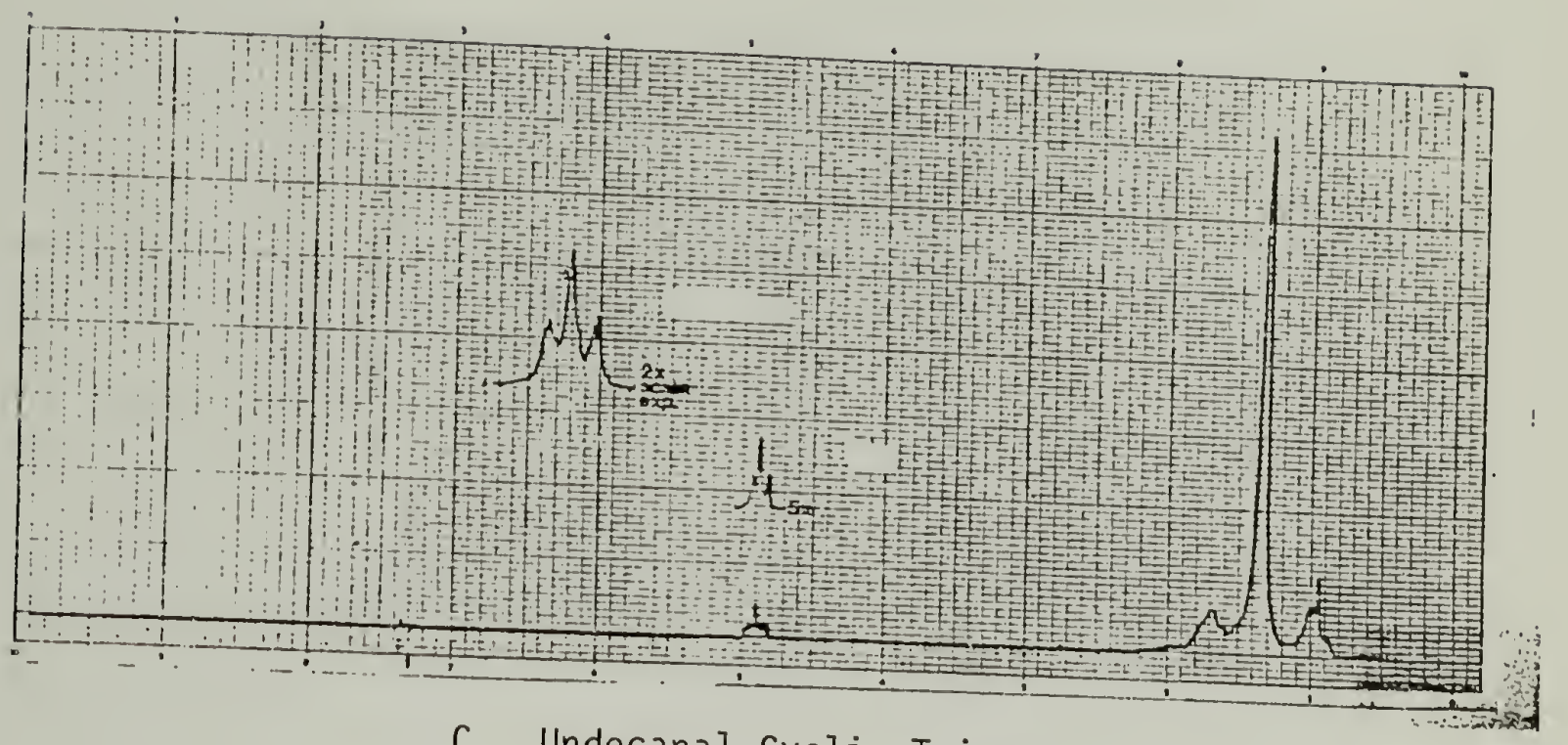


A. Nonanal Cyclic Trimer

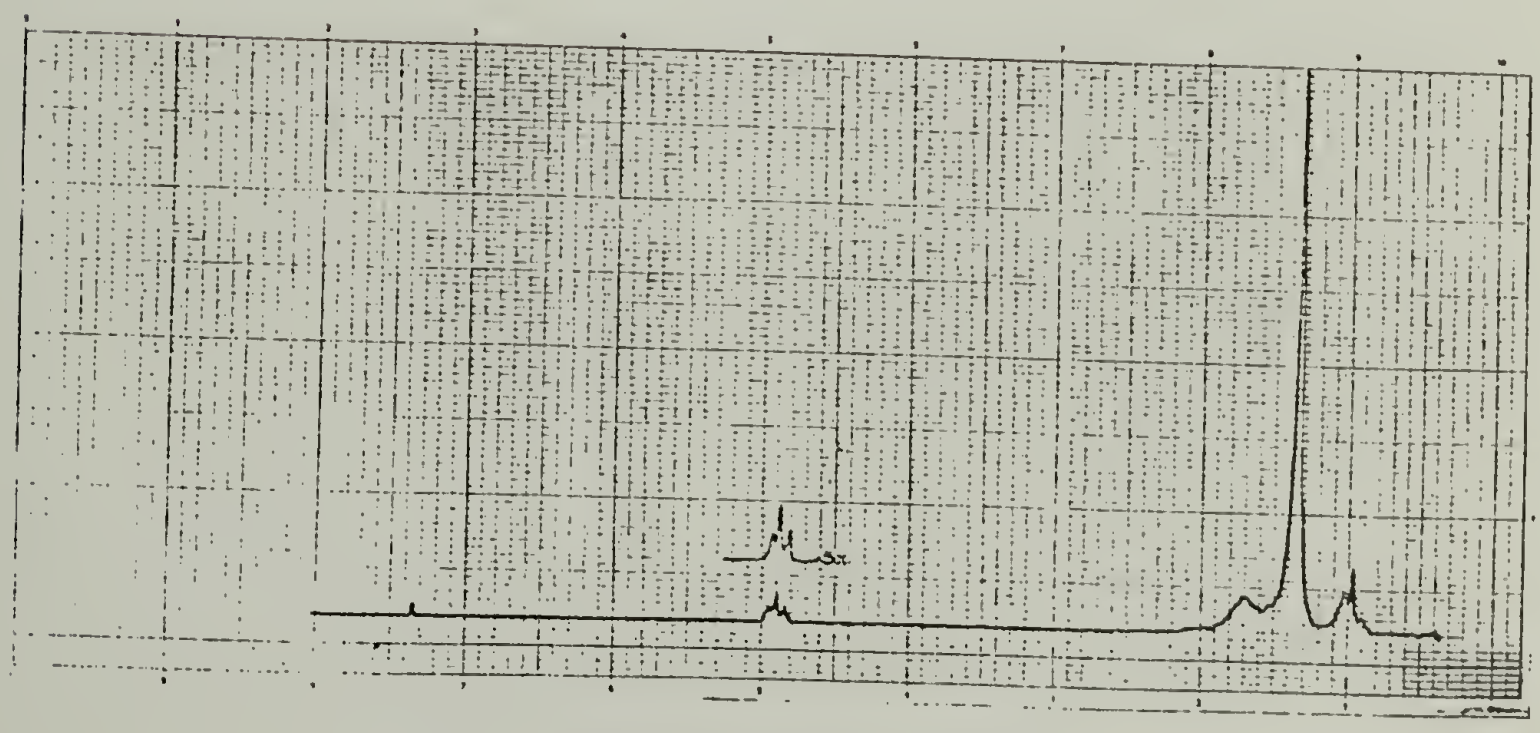


B. Decanal Cyclic Trimer

Figure 5 (cont'd):



C. Undecanal Cyclic Trimer



D. Dodecanal Cyclic Trimer

($CDCl_3$) (pg. 263) of the product were in agreement with those expected on the basis of the 2,4,6-tri-n-alkyl-1,3,5-trioxane structure of the product. Initial inspection of the PMR spectrum (60 MHz) of the product in the region of δ=4.50 - 5.50 (RC<u>H</u>O-) suggested that a mixture of the two possible geometric isomers of the trisubstituted trioxane might have been obtained because of a slight ambiguity of the triplet of the acetalic proton. However, further measurements performed with expanded scale indicated that the same value of the first order coupling constant (5.1 Hz) was obtained, within experimental error, regardless of the direction of measurement. This value agreed well with the value of the coupling constant (J=5.15 Hz) between the acetalic and methylenic protons of the all cis cyclic trimer of propionaldehyde[125].

Double resonance or spin-spin decoupling PMR experiments (90 MHz) were performed in an attempt to detect the presence of two geometric isomers in the product; the spectrum obtained in a typical experiment is shown in Figure 6. The sample was irradiated with a decoupling signal applied at various frequencies in the region corresponding to δ=1.48 to δ=1.80 and the spectrum was recorded in the region of δ=4.50 to δ=4.90. In passing from scan A to scan M (Fig. 6) the frequency of the decoupling signal was adjusted in steps equivalent to 0.25 from δ=1.48 to δ=1.80. No significant change in the PMR spectrum was ever observed. Any minor variations which were observed in the region of δ=4.50-4.90 with the decoupling frequency applied were the same as those which were occasionally observed when the spectrum was repetitively scanned in this region without application of the decoupling radiation.

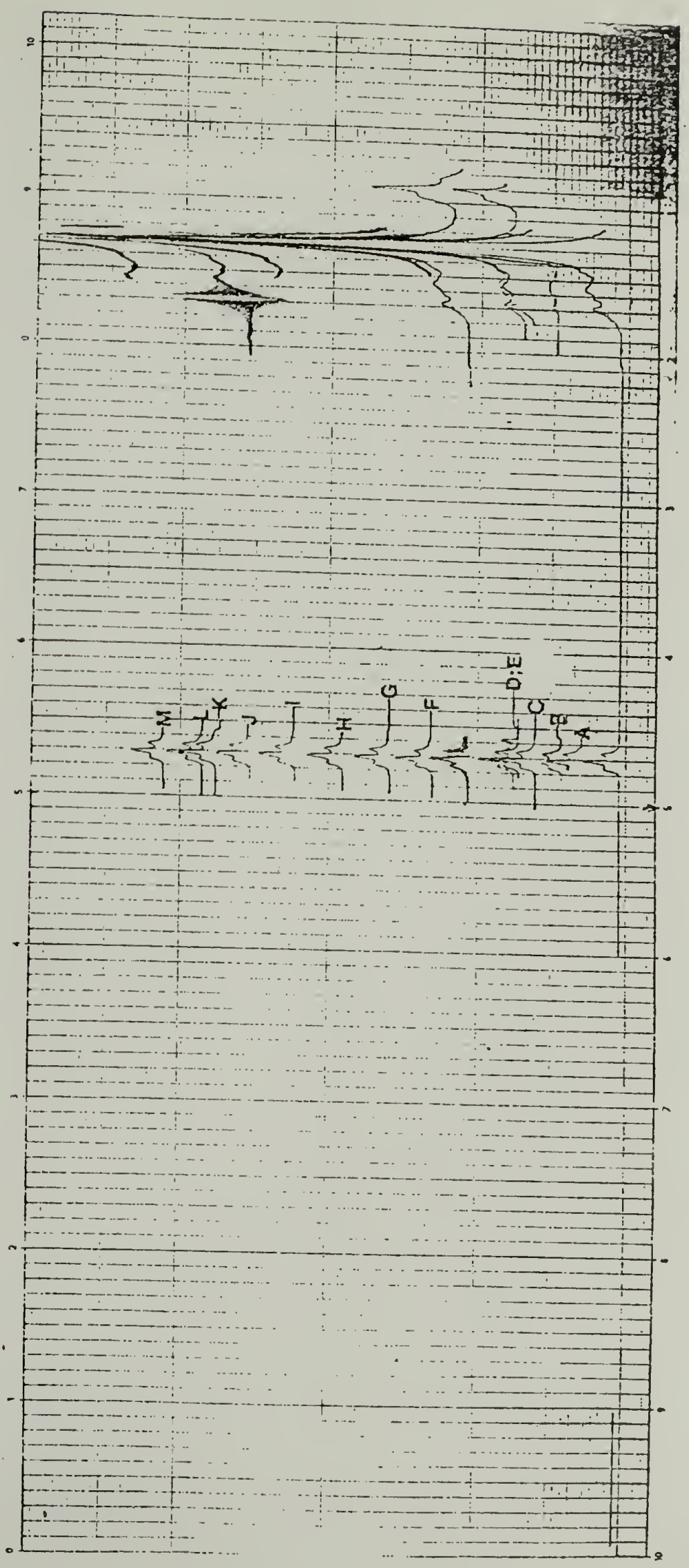


Figure 6: 90 MHz PMR of Decanal Cyclic Trimer with Spin-Spin Decoupling

Thin layer chromatography (TLC) on commercially available alumina TLC plates was employed in attempting to detect the presence of more than one specie in the product. A concentrated (1g./ml.) $CHCl_3$ solution of the product was prepared and spotted onto the TLC plates. The plates were then developed to a height of 16-17cm. in the following solvent mixtures (solvents, volume ratio, R_f of mobile component), $CHCl_3$, neat, ca. 1; $CHCl_3$:$CH_3CH(OH)CH_2CH_3$, 1:1, 0.87; $CHCl_3$:$CH_3CH(OH)CH_2CH_3$, 1:2, 0.79; EtOH:$CHCl_3$, 3:1, ca. 1. In all cases only one mobile band was observed.

Gas chromatography on a carbowax 20M column was employed for a similar purpose. The trimer was injected as its MCH solution. When the injection temperature was 190°-260°C and the column temperature was 200°-230°C only two peaks were observed with a 3-5μl. sample. The retention times of these peaks corresponded to those of MCH and monomeric aldehyde. If lower injector and column temperatures were employed, the peak having the retention time of monomeric aldehyde became progressively broader and distorted as the temperatures were lowered.

The results of the double resonance PMR experiments and the TLC experiments gave no indication that the cis-trans isomer was present in addition to the all cis isomer because the PMR spectrum in the region of δ=4.50-4.90 would consist of three closely spaced triplets if this were the case.

Although the bandwidth of the decoupling radiation employed was sufficiently narrow that simultaneous decoupling of all acetalic protons from the protons of adjacent methylene groups was not possible, it was still expected that even partial decoupling would have produced more

significant changes in the δ=4.50 - 4.90 region of the PMR spectrum if indeed both geometric isomers had been obtained in significant proportions.

The steric requirements of the long aliphatic side chains could best be accommodated with the alkyl groups in the equitorial positions about the 6-membered ring. In the cis-trans isomer at least one alkyl group would be required to occupy an axial position. Thus, on the basis of minimal steric interaction, the all cis isomer would be considered the favored isomer. It is therefore suggested that the all cis isomer of the nonanal cyclic trimer was the isomer obtained. Higher order splitting of the acetalic protons could account for complication of the spectrum in the region of question. Higher order splitting has been observed in the PMR investigation of propionaldehyde cyclic trimer[125]. Furthermore, the possibility of aggregation of the long chain molecules in solution, resulting in incomplete signal averaging and attendant loss of resolution, was also considered as a possible source of complication of the PMR spectrum of the trimer. The cyclic trimer decomposed to aldehyde under the conditions of the GC experiments and hence these experiments were of no value in investigating the isomeric purity of the product.

The infrared spectrum of decanal cyclic trimer in $CHCl_3$ solution is compared with that of other aldehyde cyclic trimers in Figure 4. The PMR (90 MHz) spectrum of the cyclic trimer of decanal ($CDCl_3$), together with that of the cyclic trimers of other higher aliphatic aldehydes, is shown in Figure 5 (B). The CMR spectrum ($CHCl_3$) of the trimer is shown in Figure 7 (B).

The thermal decomposition of decanal cyclic trimer in N_2 was investigated by TGA; the results are given in Table 4. The temperature of maximum rate of weight loss was quite similar to that observed for the cyclic trimer of nonanal.

The melting behavior of the cyclic trimer was investigated by DSC under a wide variety of conditions. Results of representative runs are given in Table 5. All annealing and quenching of the samples was performed in the calorimeter; a significant influence of thermal history upon peak temperatures and transition enthalpies was never observed. Only one endothermic transition was observed in samples of the trimer in the temperature range of -50^{o} to $+100^{o}C$. In all cases the enthalpies associated with the fusion endotherms equalled the enthalpies associated with the crystallization exotherms within the limits of experimental error.

When crystallized from solution or from the melt the trimer exhibited a pronounced tendency to crystallize in a spherulitic morphology.

4. Undecanal cyclic trimer. Undecanal cyclic trimer was prepared in 95% yield from pretreated and distilled undecanal when the reaction was conducted in diethyl ether-pentane solvent with $SbCl_5$ catalyst. The product precipitated during the reaction and was readily isolated. Trimerization of undecanal in bulk with H_2SO_4 catalyst was less successful, the isolation of the trimer being more difficult. The crude product prepared with $SbCl_5$ catalyst was soluble in $CHCl_3$. The product was easily recrystallized from a diethyl ether-ethanol mixture.

The infrared spectrum (KBr) (pg. 256) and the PMR spectrum ($CDCl_3$) (pg. 264) were in agreement with those expected on the basis of the

TABLE 4

Thermogravimetric Analysis of 2,4,6-Tri-n-alkyl 1,3,5-trioxanes (Aldehyde Cyclic Trimers)[a]

n-Alkyl Group	$T^{b}_{5\%}$ (in ^{o}C)	T^{c}_{max} (in ^{o}C)
Octyl	220	276
Nonyl	219	274
Decyl	247	294
Undecyl	182	239

[a]At 20^{o}C/min. in N_2. Trimers were twice recrystallized from a diethyl ether-ethanol mixture.

[b]Temperature at which 5% weight loss had occurred.

[c]Temperature of maximum negative slope of TG curve (MDT).

TABLE 5

Melting Temperatures and Heats of Fusion of 2,4,6-Tri-n-alkyl-1,3,5-trioxanes by DSC[a]

n-Alkyl Group	Conditions	MP[b] (in °C)	Peak Temperatures (in °C)	H_f (±3%) (in $\frac{cal.}{g.}$)	(in $\frac{kcal.}{g.}$)
Octyl	Virgin	36	36	42.4[c]	17.9[c]
"	Quenched after first melting	-	35	41.2[c]	17.5[c]
"	Annealed at 36°C for 30 min.	-	36	43.7	18.3
Nonyl	Virgin	48	46	49.3[c]	22.9[c]
"	Annealed at 44°C for 20 min.	-	47	50.1	23.4
Decyl	Virgin	56	55	52.3[c]	26.5[c]
"	Quenched after first melting	-	55	52.6[c]	26.8[c]
"	Annealed at 54°C for 30 min.	-	56	52.0	26.5
Undecyl	Virgin	63	61	53.1[c]	29.3[c]
"	Quenched after first melting	-	61	52.5[c]	28.8[c]

TABLE 5 (cont'd)

[a]At 10°C/min.. Trimers twice recrystallized from diethyl ether-ethanol mixture.

[b]Hot stage microscope at 2°C/min..

[c]Average of duplicate determinations.

2,4,6-tri-n-alkyl-1,3,5-trioxane structure of the product. Absorption bands assignable to fundamental deformations of C-H bonds were clearly evident and dominated the infrared spectrum. Two bands in the general frequency region of C-C and C-O skeletal vibrations, near 1160 and 1120cm.$^{-1}$, were assigned to C-O stretching in the acetal structure.

The PMR spectrum of undecanal cyclic trimer was quite similar to that of decanal cyclic trimer. Because of the low relative number of acetalic protons per trimer molecule the PMR signal of these protons is proportionally weaker and this situation seriously impeded attempts to investigate the isomeric purity of the samples by PMR.

The trimer was also investigated by TLC and GC. In TLC experiments a concentrated (1g./ml.) solution of the trimer was spotted onto the TLC plates which were then developed as in the case of decanal cyclic trimer; (solvents, volume ratio, R_f of mobile component), $CHCl_3$, neat, ca. 1; $CHCl_3$:$CH_3CH(OH)CH_2CH_3$, 1:1, 0.85; $CHCl_3$:$CH_3CH(OH)CH_2CH_3$, 1:2, 0.72; EtOH:$CHCl_3$, 1:1, ca. 1. The trimer was also examined by GC precisely as discussed in the case of decanal cyclic trimer; the results of the TLC and GC experiments were completely analogous to those discussed for decanal cyclic trimer.

The infrared spectrum of undecanal cyclic trimer, in $CHCl_3$ solution, is compared with that of other higher aliphatic aldehyde cyclic trimers in Figure 4. The PMR (90 MHz) spectrum of undecanal cyclic trimer, together with that of other higher aliphatic aldehyde trimers, is shown in Figure 5 (C). The CMR spectrum of the trimer is shown in Figure 7 (C) (pg. 142).

The thermal decomposition of undecanal cyclic trimer in N_2 was

investigated by TGA; the results are given in Table 4. The temperature of maximum rate of weight loss was similar to that of the cyclic trimers of nonanal and decanal. The type and amount of impurities present in samples must be considered when comparing their thermal decomposition behavior. If the level of impurities in the undecanal cyclic trimer was indeed lower, resulting in a slightly lower rate of production of volatiles, this difference would be accentuated by a slightly lower rate of volatilization of the decomposition products. If the intrinsic thermal stability of all samples were similar, then the observed rate of weight loss would be more influenced by the rate of volatilization of the decomposition products.

The melting behavior of undecanal cyclic trimer was investigated by DSC under a wide variety of conditions. Results of some representative runs are given in Table 5. All annealing and quenching of the samples was performed in the calorimeter; a significant influence of thermal history upon the peak temperatures and transition enthalpies was never observed. Only one endothermic transition was observed in samples in the temperature range of -50^{o} to $+100^{o}C$. Within the limits of experimental error the enthalpies associated with fusion endotherms always equalled the enthalpies associated with crystallization exotherms.

When crystallized from solution or from the melt the trimer showed a pronounced tendency to crystallize in a spherulitic morphology; similar to the trimers of nonanal and decanal.

5. Dodecanal cyclic trimer. Dodecanal cyclic trimer was prepared in a cryde yeild of 23% by the $SbCl_5$ catalysed reaction of dodecanal in

diethyl ether-pentane solvent. Although the product was isolated directly from the reaction mixture the yield was considerably lower than was expected on the basis of the results of the experiments with decanal and undecanal. The trimer was easily recrystallized from a diethyl ether-ethanol mixture. The infrared spectrum (KBr) (pg. 256) and the PMR spectrum ($CDCl_3$) (pg. 265) were consistent with the 2,4,6-tri-n-alkyl-1,3,5-trioxane structure of the product. The general appearance of the spectra were very similar to those recorded for other higher aliphatic aldehyde cyclic trimers.

The infrared spectrum of a $CHCl_3$ solution of the trimer of dodecanal, together with those of other higher aliphatic aldehyde cyclic trimers, is shown in Figure 4 (D). By far the strongest and most predominant absorptions were recorded in the region of 2980 to 2820cm.$^{-1}$, the strongest absorptions were at 2925 and 2860cm.$^{-1}$. These absorptions were invariant from one cyclic trimer to the next and were assigned to C-H stretching in methylene groups of the long aliphatic chains. A shoulder was recorded on each of these two bands and was most clearly seen in the spectrum of nonanal cyclic trimer. The position of these shoulders near 2960cm.$^{-1}$ (on peak at 2925cm.$^{-1}$) and near 2870cm.$^{-1}$ (on peak at 2860cm.$^{-1}$) was quite stable in the series and these absorptions were assigned to C-H stretching in the terminal methyl groups of the long aliphatic chains. Moderate to weak absorptions resulting from various C-H bending modes were recorded in the region of 1480 to 1340cm.$^{-1}$, the most predominant band in this region was recorded at 1470cm.$^{-1}$ (δ_s; CH_2). Moderate to strong absorptions were recorded at 1150 and 1120cm.$^{-1}$ and these were assigned to stretching of skeletal

C-O bonds in the trisubstituted trioxane structure.

The PMR spectrum (90 MHz) of dodecanal cyclic trimer (in $CDCl_3$), together with those of other higher aliphatic aldehyde cyclic trimers, is shown in Figure 5. The PMR spectra for all the trimers were very similar. The weak absorption recorded in the region of δ=4.60-4.80, which appeared as a triplet, was assigned to the acetalic protons bound to the carbon atoms of the trioxane ring. As expected, the apparent relative intensity of this absorption decreased as the length of the alkyl group increased. The relatively weak intensity of the signal in this region impeded the detailed investigation of the samples by PMR spectroscopy. PMR experiments conducted with 2X to 5X scale expansion and, in some instances, decoupling experiments, both gave no strong indication of overlapping triplets in the region of the spectra in question. The occurrence of higher order splitting has already been cited as a possible explanation for the more complicated appearance of the weak signals of the acetal protons. The strong absorption recorded in the spectra near δ=1.25 was assigned to the protons on the interior methylene groups of the n-alkyl substituents of the trioxane ring. The shoulder on the low field side of this absorption was assigned to the protons of the methylene group directly attached to the carbon atom of the trioxane ring. The resonance absorption of the protons once removed from the trioxane ring might have also contributed to this shoulder.

The PMR signal near δ=0.90 was assigned to the terminal methyl group of the n-alkyl group. As expected the apparent relative intensity of this signal decreased as the length of the alkyl group increased in

the same way as the signal of the acetalic protons. The general appearance of this absorption signal was identical to that normally observed for the terminal methyl group of long chain compounds[126].

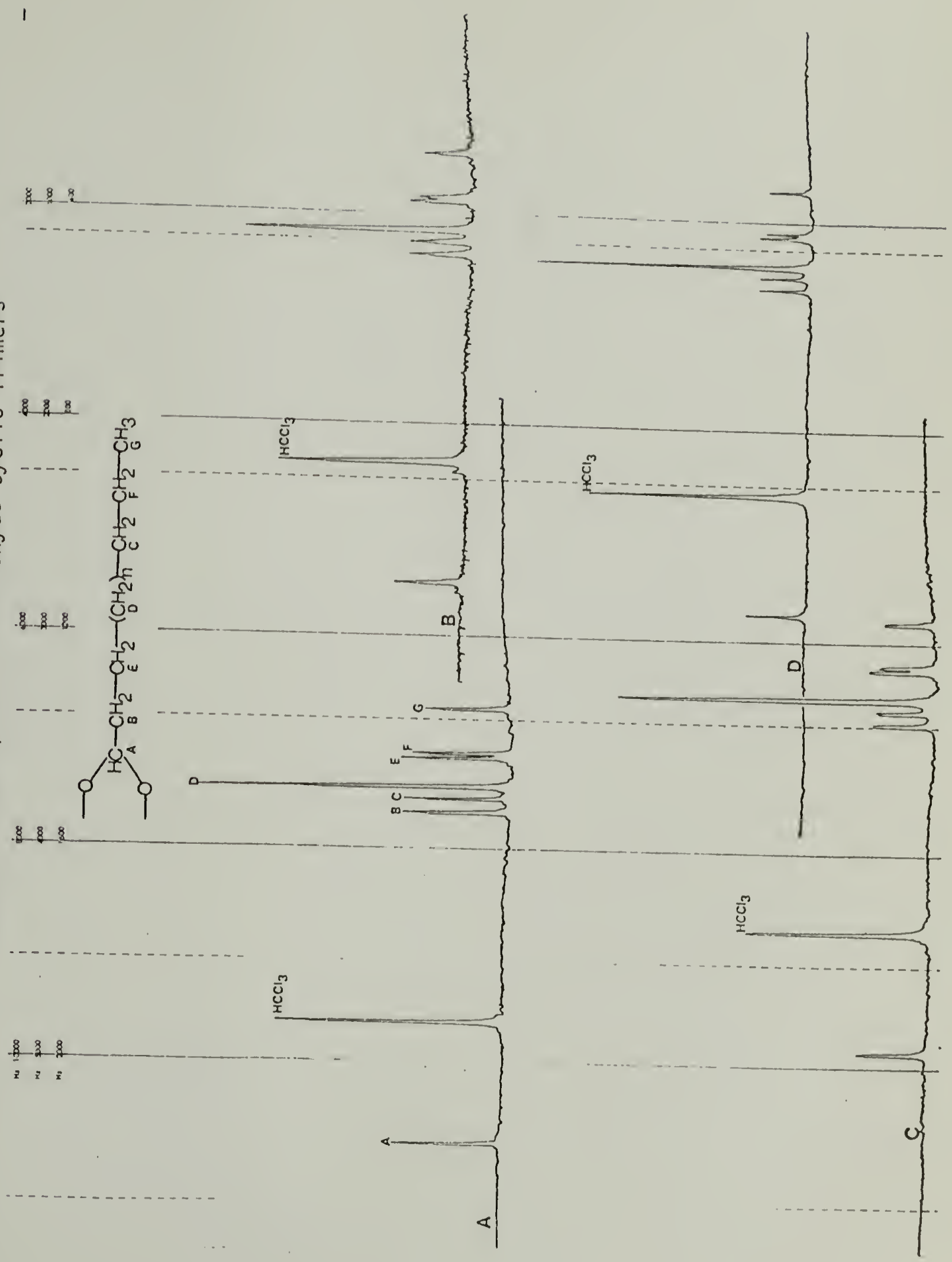
The CMR spectrum of dodecanal cyclic trimer is compared with that of other higher aliphatic aldehyde cyclic trimers in Figure 7. Seven distinct signals were recorded in each spectrum. As indicated in the figure the resonance absorptions of all but one carbon atom occurred at higher field than that of the $CHCl_3$ standard. The resonance absorption of the interior methylene groups (3 to 6) showed as a single absorption. The CMR spectra gave no evidence of the presence of more than one geometric isomer in the samples.

The thermal decomposition of dodecanal cyclic trimer in N_2 was investigated by TGA; the results are given in Table 4. It was noted that the temperature of maximum rate of weight loss recorded for this trimer was significantly lower than that recorded for any of the other three trimers investigated. It is believed that this was due to a higher level of impurities in this trimer as compared to the others.

If the dodecanal cyclic trimer was dissolved in $CHCl_3$ and this solution was washed with $NaOH_{aq}$ and distilled water, then the temperature of maximum rate of weight loss of the trimer recovered from this solution and recrystallized resembled more closely that of the other trimers (280^oC). This observation supports the suggestion that the lower temperature of maximum rate of weight loss originally observed for dodecanal cyclic trimer was due to a higher level of impurities in this trimer.

The melting behavior of dodecanal cyclic trimer was investigated

Figure 7: CMR Spectra of Aldehyde Cyclic Trimers



by DSC under a wide variety of conditions, the results of typical runs are given in Table 5. All annealing and quenching of samples was performed in the calorimeter; a significant influence of thermal history upon peak temperatures and transition enthalpies was never observed. As seen in Table 5 the largest step increase in melting point (hot stage microscope) and peak temperature (DSC) was observed between nonanal and decanal cyclic trimers. Similarly, the largest step increase in the heat of fusion (in cal./g.) was observed between the same two cyclic trimers. The step increases in melting points, peak temperatures, and transition enthalpies observed between the other trimers were more similar. The melting points of the trimers fall in the same general temperature region in which melting and various polymorphic transitions are observed for certain other types of long chain compounds, particularly glycerides of fatty acids[127]. This observation is perhaps no accident but reflects the influence of the long alkyl groups on the crystallization of the various types of compounds. As will be discussed later, polymers of higher aliphatic aldehydes also exhibit thermal transitions in the same general temperature region.

In general only one endothermic transition was recorded for samples of dodecanal cyclic trimer in the temperature range of -50^{o} to $+100^{o}C$. In some DSC scans recorded for virgin samples of dodecanal cyclic trimer a very small peak was recorded near $66^{o}C$ in addition to the main peak at $61^{o}C$. This peak was never observed in thermograms once the sample had been melted in the calorimeter, regardless of the thermal history of the sample.

C. Polyhexanal (PHXA)

1. Introduction. This experiment was conducted to verify the general efficacy of stabilization of aliphatic aldehyde polymers having longer side chains by the technique of endcapping with acetic anhydride. Hexanal was chosen for this experiment for two reasons. This monomer is sufficiently volatile (b.p.=128^{o}C) so that the TGA curve of the polymer should more truly reflect the degradation of the polymer and not the rate of volatilization of degradation products which have a boiling point above the limit of thermal stability of the polymer. Secondly, the length of the side chain of hexanal is sufficiently long that polymers of hexanal exhibit the phenomenon of side chain crystallization[75]. The various factors which contribute to this behavior might also be important in the endcapping reaction.

In conjunction with this experiment, but for a different purpose, the extraction of LTB with MCH was investigated to assess the suitability of the method used to prepare LTB initiator solution for use in the polymerization of higher aliphatic aldehydes. The initiator solutions were prepared by weighing a quantity of fresh LTB sublimate (assumed to be pure LTB) into a volumetric flask and diluting to volume with dry MCH. It was believed that an initiator solution whose concentration was known to at least 2 significant figures could be prepared by this procedure, which would be quite adequate for preparative scale polymerization.

2. Polymerization of hexanal, endcapping of the polymer, and TGA of the product. Hexanal was polymerized in MCH at -78^{o}C with 2 mole%

LTB initiator. Hexanal of adequate purity for these experiments was obtained by pretreating hexanal as described followed by a single distillation and treatment of the distillate with molecular sieves. The monomer was added to the cold (-78°C) mixture of initiator and solvent; the concentration of monomer with respect to solvent was 20%. In a blank experiment monomer and solvent, at this same concentration, formed a homogeneous solution at -78°C.

After the polymerization was allowed to proceed overnight a chilled mixture of acetic anhydride and pyridine was added to the cold polymerization mixture. The reaction mixture was allowed to warm to room temperature and an aliquot of the mixture, which contained a number of gel particles, was withdrawn and poured into acetone. The polymer isolated in this experiment (6% yield based on monomer, 13% of total yield) was washed with acetone and dried at reduced pressure over KOH. Acetone was added to the remainder of the reaction mixture and the end-capping reaction was allowed to proceed at 60° to 120°C for 1 hr. during which time the polymer did not dissolve but became highly swollen and 100ml. of volatiles was collected. The polymer recovered by filtration of the hot reaction mixture (40% yield based on monomer, 87% of total yield) became harder and opaque with repeated acetone washing and was subsequently treated exactly as the polymer isolated before the end-capping procedure was completed.

The TGA curves of the two samples are compared in Figure 8. A weight loss was already registered for the uncapped sample near 80°C, whereas no noticeable weight loss was observed for the more completely capped sample until a temperature near 120°C had been reached. Although

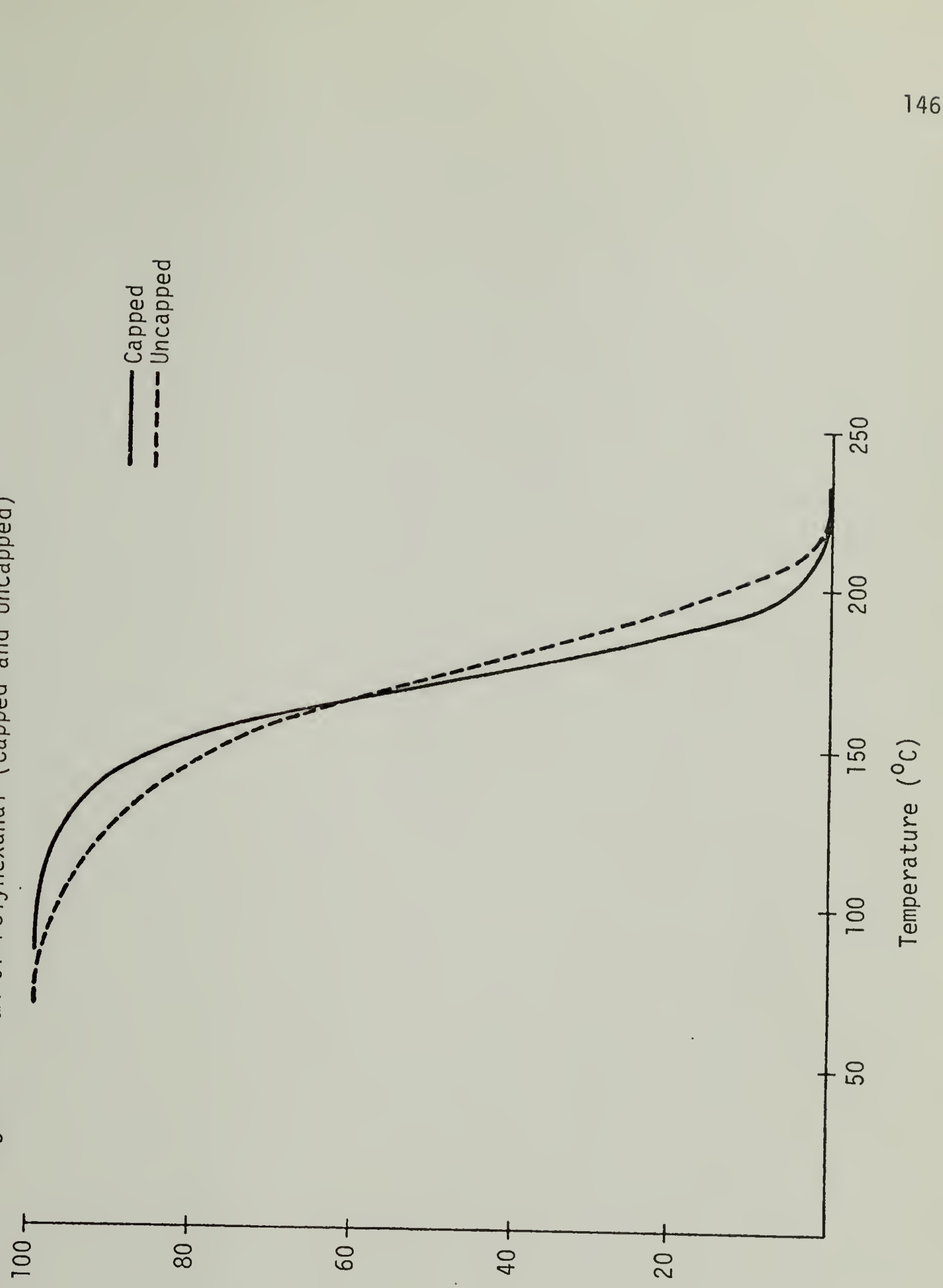


Figure 8: TGA of Polyhexanal (Capped and Uncapped)

the TGA curve of the uncapped sample was broader than that of the more completely capped sample, the temperature of maximum negative slope of the TGA curve (MDT) was similar for both samples. The TGA curve of the more completely capped sample was sharper than that of the uncapped sample. This observation probably resulted from two effects. First, a degradation of molecular weight probably occurred when the endcapping was conducted at elevated temperatures resulting in a higher concentration of endgroups in the more completely capped sample. Second, there was probably a disparity in the level of impurities between the two samples; the more completely capped sample having the lower level of impurities. The results of the TGA experiments indicated that stabilization of aliphatic aldehydes with longer side chain length by treatment with acetic anhydride/pyridine was possible and that it was probably feasible to attempt this technique with polymers of higher aliphatic aldehydes.

The higher stability of the more completely capped sample was verified by visual observation of the "shelf-life" of the samples. Both samples were stored at room temperature in the dark in open containers. Within two weeks the originally solid white sample of uncapped polymer had transformed into a yellow oil which primarily consisted of hexanal and hexanoic acid. The appearance of the more completely capped sample was unchanged after 6 months of storage; only a faint odor of hexanal was detected in the sample after this time.

3. Extraction of LTB with MCH. Titration of the aqueous washings of the MCH extract of samples of LTB showed that a good correlation existed between the amount of MCH extractable base in the LTB and the

yield of sublimate from the samples. This suggested that, of the various species present in crude samples of LTB, only the alkoxide is sublimed from the sample and its solubility is greater than that of any other species. These observations allowed greater confidence to be placed in the method used to prepare the initiator solutions.

D. Polynonanal (PNA)

1. Introduction. A number of experiments were conducted to investigate the polymerization of nonanal. The most pertinent of these experiments were described in detail in Chapter II and will be discussed in this section. All experiments were conducted with the objective in mind of preparing polymer in sufficient amount and with sufficient stability for preliminary investigation of the properties of the polymer, particularly its melting behavior.

Two sets of exploratory scale polymerization experiments were conducted. One set was carried out using MCH solvent and initial monomer concentrations of 0.6M to 0.9M with 2 mole% LTB initiator; the monomer was undistilled. Another set was carried out using n-hexane solvent at initial monomer concentrations in the range of 0.1M to 0.9M and 5-10 mole% LTB; the monomer was distilled once. Two preparative scale polymerization reactions were successfully carried out. In one such experiment a procedure very similar to one which was known to be successful for the polymerization of heptanal was followed[22]; the polymer was endcapped with acetic anhydride at elevated temperatures. In a second experiment an improved procedure was used which involved controlled cooling of the polymerization mixture. The preparative scale

polymerizations will be discussed later in more detail.

In both sets of exploratory scale polymerizations the LTB initiator was added as its MCH solution to a solution of monomer in the desired solvent after the solution had been cooled to -18° to -22°C. This order of charging had previously been found to result in significantly lower yields of polymer in the case of the lower aliphatic aldehydes when the charging temperature was below -50°C; probably as the result of occlusion of initiator by the polymer which formed rapidly[21]. In the experiments reported here the charging was at a temperature which was expected to be near the threshold temperature of the polymerization so that rapid polymer formation was not expected to be as serious a problem. In the polymerization of higher melting aliphatic aldehydes with longer alkyl chains the miscibility of the components of the polymerization mixture is an important factor which affects the mixing of the components . Monomer precipitated at the charging temperature in both sets of exploratory reactions. The problem of monomer precipitation was more significant when n-hexane was the solvent (phase separation at -20°C at ca. 0.5M monomer) than when MCH was the solvent (phase separation at -20°C at ca. 0.9M monomer). Although polymer was never obtained from any of the exploratory reactions in sufficient amount, a small amount was obtained from some polymerizations in n-hexane. This observation suggested that, as expected, both monomer purity and monomer solubility were important factors to be considered if polynonanal was to be prepared in workable yield. (In both sets of exploratory reactions the purity of the solvent and initiator was such that these were suitable for use in the polymerization of chloral.) From consideration of the

results of the exploratory polymerization and comparison with the known aspects of aldehyde polymerization it was recognized that adequate control of purified monomer concentration, solvent nature, and reaction temperature history would have to be exercised in preparative scale polymerizations.

As mentioned previously two techniques were employed for the polymerization of nonanal to crystalline polymer. Polymer was obtained in the highest yield with the highest inherent viscosity when the temperature history of the polymerization reaction was carefully controlled. The technique of endcapping with acetic anhydride was effective for the stabilization of polynonanal. Both polymers had the same chemical structure and very similar crystal structures, and exhibited a dual melting behavior or double melting point. Polynonanal could be extruded into filaments at a temperature near or above the first melting point. Analysis of the x-ray diffraction diagrams indicated that polynonanal is capable of existing in a crystal structure which is completely analogous to one which has been established for polyheptanal.

2. Synthesis and characterization of PNA.

a. Synthesis and chemical characterization. Two slightly different procedures were successfully employed for the preparation of polynonanal. In the first procedure, which was very similar to the procedure which has been used for the anionic polymerization of heptanal and octanal, freshly distilled nonanal was injected into a mixture of MCH and LTB which had been chilled to -58° to -60°C. If the temperature of the solvent / initiator mixture was lower (e.g. -72°C) no polymer

was obtained. It is believed that if the temperature of the solvent / initiator mixture is too low then monomer immediately crystallizes when injected and does not pass into solution, therefore, polymerization is prevented[77]. When nonanal was injected into the cold solvent / initiator mixture at somewhat higher temperatures some crystallization of monomer occurred, however, a sufficient amount of monomer was in solution such that polymerization proceeded. After a period of 20 min. the viscosity of the polymerization mixture had increased considerably and the polymerization was assumed to be substantially complete. The polymerization mixture was then kept overnight at -78^{o}C. A chilled mixture of acetic anhydride and pyridine, as well as acetone, was added to quench the polymerization and to endcap the polymer. The reaction mixture was then warmed to room temperature and the suspension of small gel-like particles was subsequently heated to a temperature of 125^{o}C in order to accelerate and force the endcapping reaction. The secondary hydroxyl groups of the polymer chain ends are shielded by the long alkyl side chain and hence are less reactive. Therefore, polymer degradation during the heterogeneous endcapping reaction is unavoidable. Polynonanal (PNA) was isolated directly by filtration from the hot reaction mixture. Polynonanal, obtained in 35% yield by this procedure (PNA-I), had an inherent viscosity of 1.06dl./g. at 66^{o}C (in tetralin).

In the second procedure (Procedure II) freshly distilled nonanal was injected into a solvent / initiator mixture which was maintained at -20^{o}C, a temperature which was expected to be near or above the threshold temperature of the polymerization yet low enough that base catalysed side reactions of the aldehyde were suppressed. When the

bath temperature was lowered to -50°C the formation of some gel particles and a general thickening of the polymerization mixture (ca. 1M in monomer) was observed as the bath temperature cooled to near -46°C. As the bath temperature was brought to near -55°C the polymerization mixture became very stiff and difficult to stir. In addition to polymerization, some monomer precipitation was also observed; the polymerization was assumed to be substantially complete at this time. The polymerization mixture was allowed to sit overnight at -78°C. A chilled mixture of acetic anhydride and pyridine was added to the polymerization mixture in order to quench the polymerization and endcap the polymer. In this procedure the endcapping reaction was conducted for several hours at or below room temperature. It had been reported that the rate of polymer degradation more effectively competes with the rate of the endcapping reaction when the endcapping reaction of polyaldehydes having longer side chains was conducted at elevated temperatures[77]. Polynonanal prepared by this second procedure (PNA-II) was obtained in a very highly swollen state. Polyaldehydes, as they are prepared, typically retain a significant portion of absorbed monomer which may be separated from the polymer with acetone[25].

In the case of anionically prepared polyaldehydes having longer side chains (e.g. polynonanal) swelling of the polymers by solvents, as well as monomer, is another impediment to facile isolation of the polymers. The addition of acetone to the reaction mixture appeared to deswell the polynonanal to a certain extent and aided the filtration of the reaction mixture. However, the polymer still retained some monomer and solvent. Because the polymer remained swollen during the

lengthy filtration process, some polymer degradation, which is facilitated when the polyaldehyde is dissolved or swollen, undoubtably occurred during the isolation procedure. The yield of crude, wet PNA-II was high but after drying overnight in the vacuum desiccator the yield of polymer was 38%. Only a portion of this decrease in weight of product could be attributed to a loss of adsorped monomer during the drying. The majority of the decrease in yield was believed to be due to degradation of the polymer which was not sufficiently stabilized during the endcapping reaction. The inherent viscosity of the polymer, after acetone washing and redrying, was 2.9dl./g. at 61^{o}C (in tetralin).

In both procedures the polymer appeared as a highly swollen gelatinous mass before the addition of the endcapping reagent; analogous to polyheptanal prepared in MCH with LTB initiator[21]. Qualitatively speaking, the solubility characteristics of PNA-I and PNA-II were the same and, in general, PNA was more soluble in common organic solvents than PHA prepared under similar conditions.

The infrared spectra of PNA-I (pg. 257) and PNA-II (pg. 258) were very similar to each other and indicated that both polymers had the same polyacetal structure. Absorptions in the region of 3300 to 3500cm.$^{-1}$ (O-H) were more clearly evident in the infrared spectrum of PNA-II which indicated that, as expected, this sample of PNA was less completely endcapped.

The PMR spectra of PNA-I and PNA-II (pg. 266 and pg. 267 respectively) were identical and gave further indication of the polyacetal structure of the polymers. Furthermore both samples of PNA could be degraded by 2,4-dinitrophenylhydrazine reagent; the melting point of

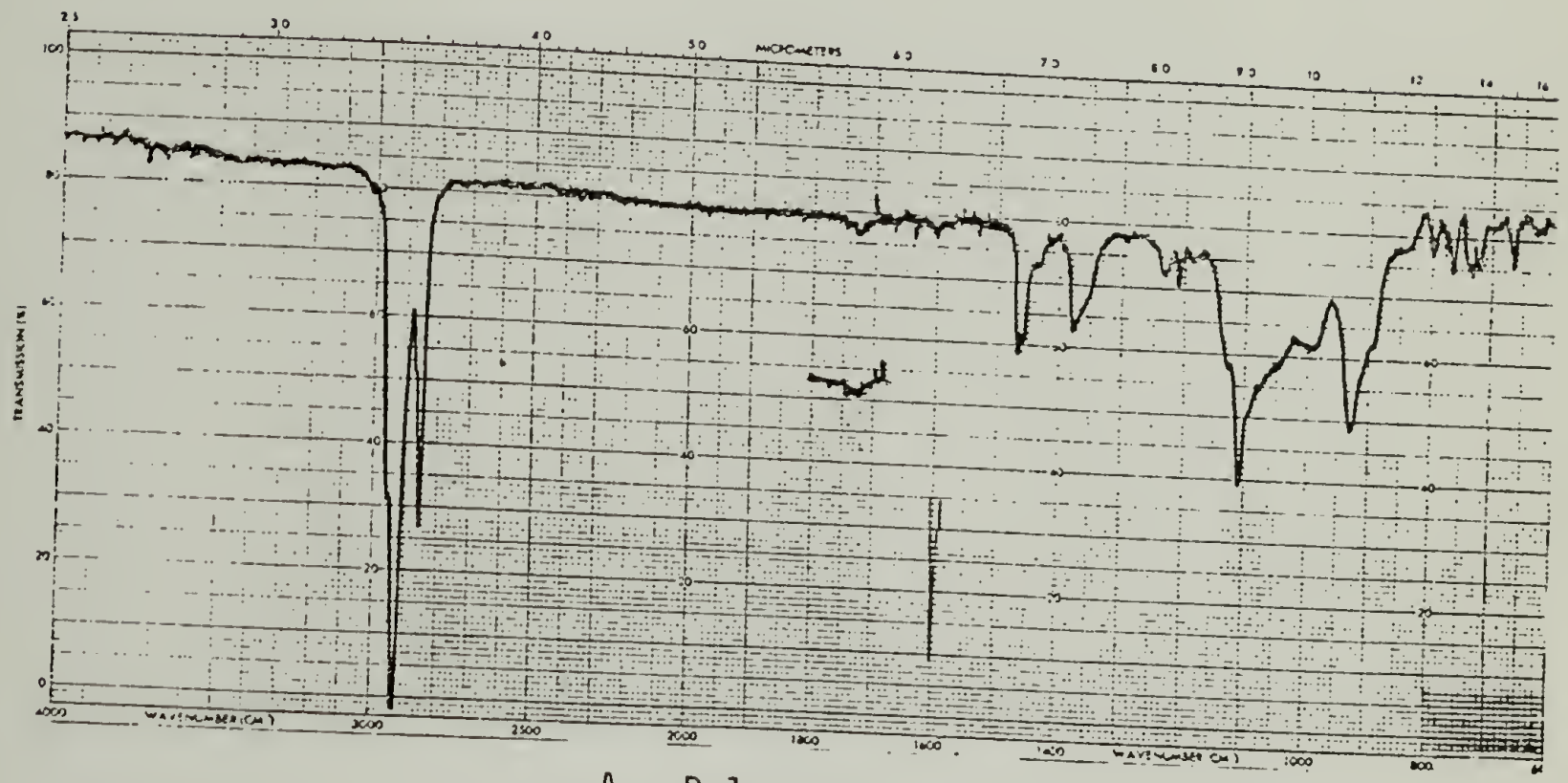
the hydrazone obtained from PNA-I was the same as that obtained from PNA-II (101^{o}-102^{o}C).

The infrared spectrum of a $CHCl_3$ solution of PNA-II is shown in Figure 9 (pg. 155). Before the spectrum was recorded PNA-II had twice been washed with acetone and dried in vacuo. The spectrum of the polymer was very similar to that of nonanal cyclic trimer, particularly in those regions where absorptions due to fundamental deformations of C-H bonds were recorded. In such regions the infrared spectrum of the polymer was superimposable upon that of the trimer. The most significant differences between the spectrum of polymer and cyclic trimer were in the region of 1150 to 900cm.$^{-1}$. The differences in the spectra in this region indicated differences in the C-O skeletal stretching modes between polymer and cyclic trimer. Only a weak absorption near 1720cm.$^{-1}$ ($\nu_{C=O}$), but no O-H absorption, was found in the solution spectrum of the polymer. These observations indicate that the sample of PNA used in the infrared measurement had a reasonably high DP_n. The long alkyl polymer side chains comprise a high relative weight percent of the polymer sample (ca. 90%) and absorptions due to deformation of bonds in the side chain tended to dominate the spectrum of the polymer.

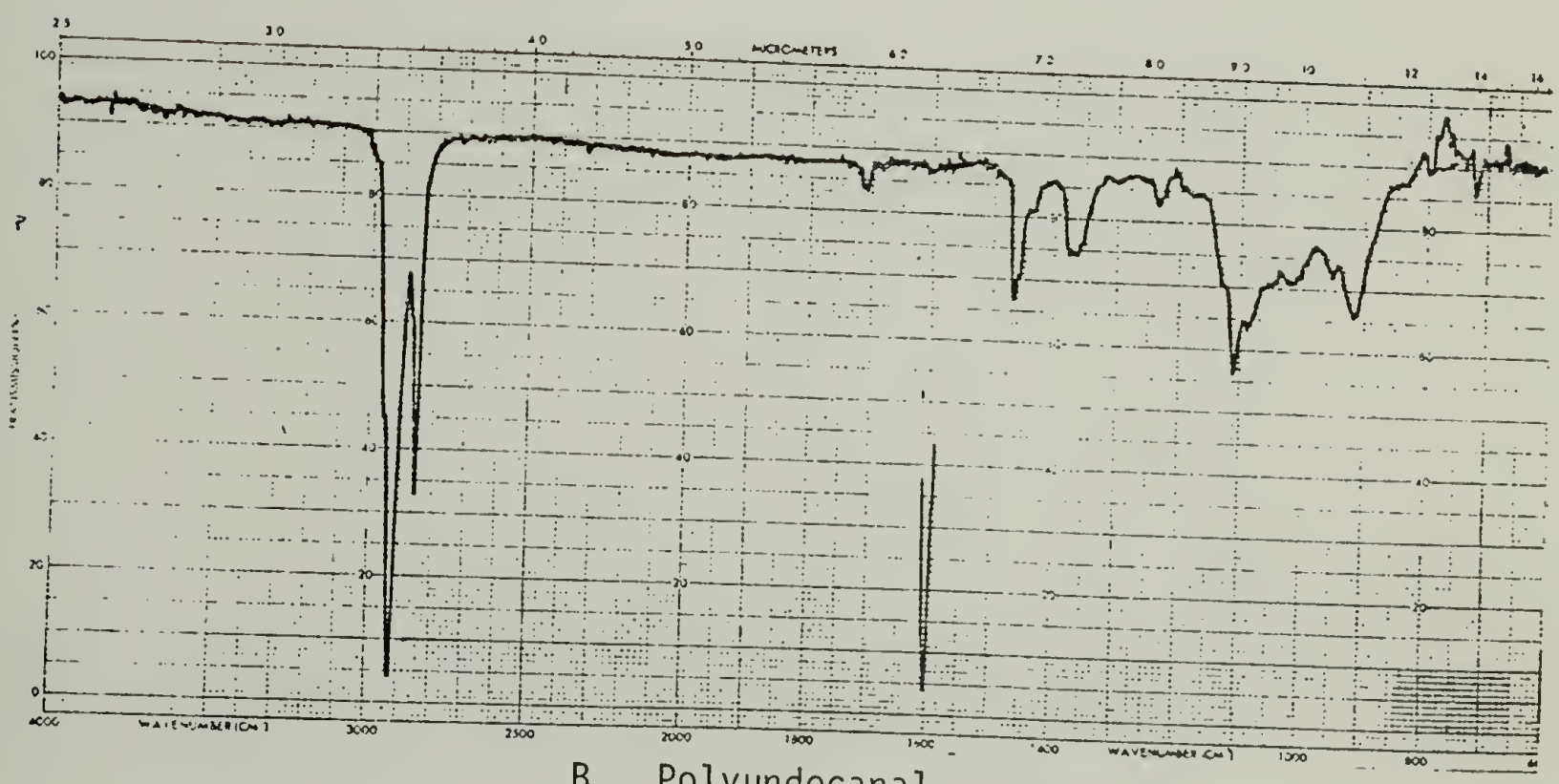
The PMR spectrum (90 MHz) of PNA-II (Figure 10) was quite similar to that of nonanal cyclic trimer and indicated the similarity in chemical structure between the two species. The most notable difference between the spectrum of polymer and trimer was the width of the signal lines, particularly in the region of δ=4.5-5.0, which were greater in the polymer spectrum. The broadening of the signals in the PMR spectrum of the polymer was thought to be due to conformational rigidity of the

Figure 9:

I.R. Spectra of Higher Aliphatic Polyaldehydes in $CHCl_3$

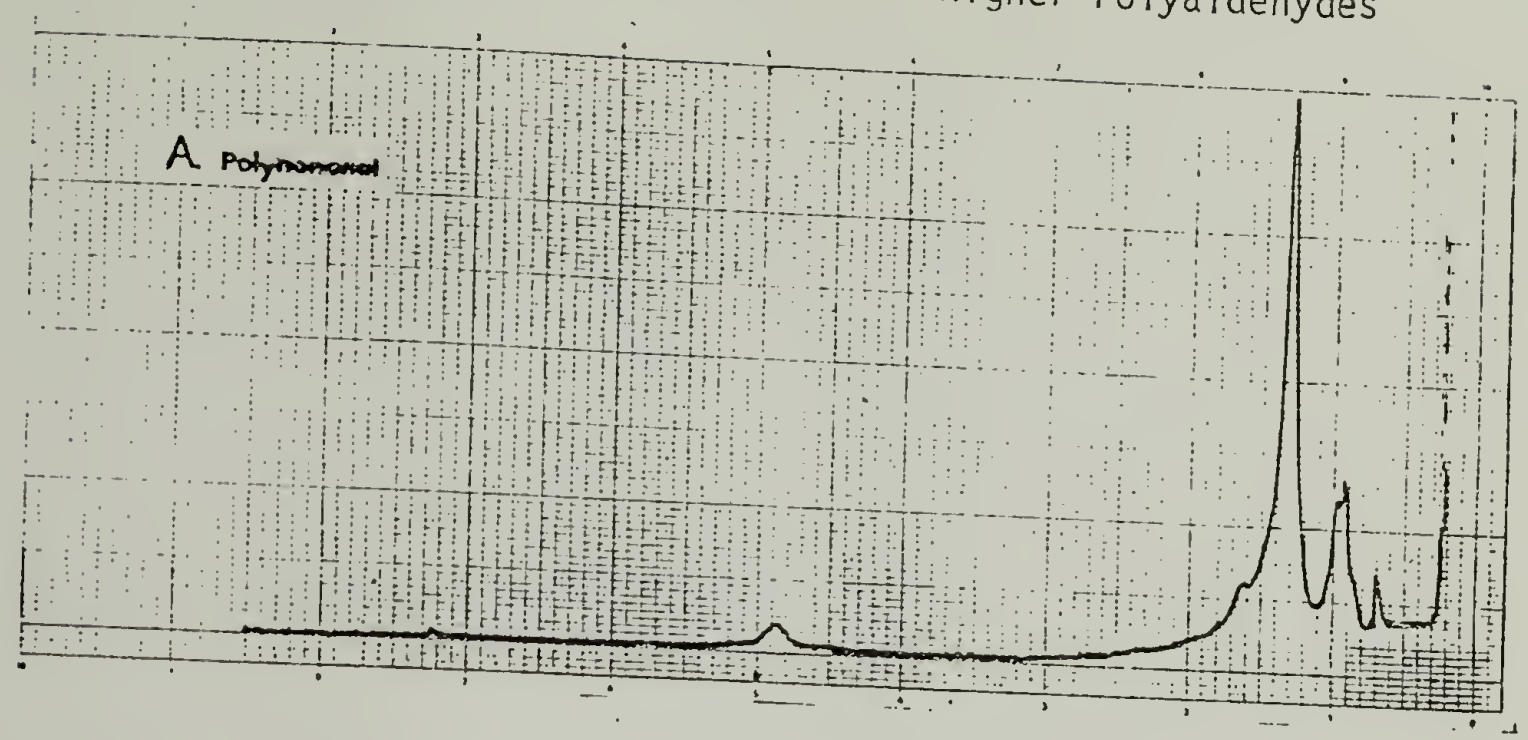


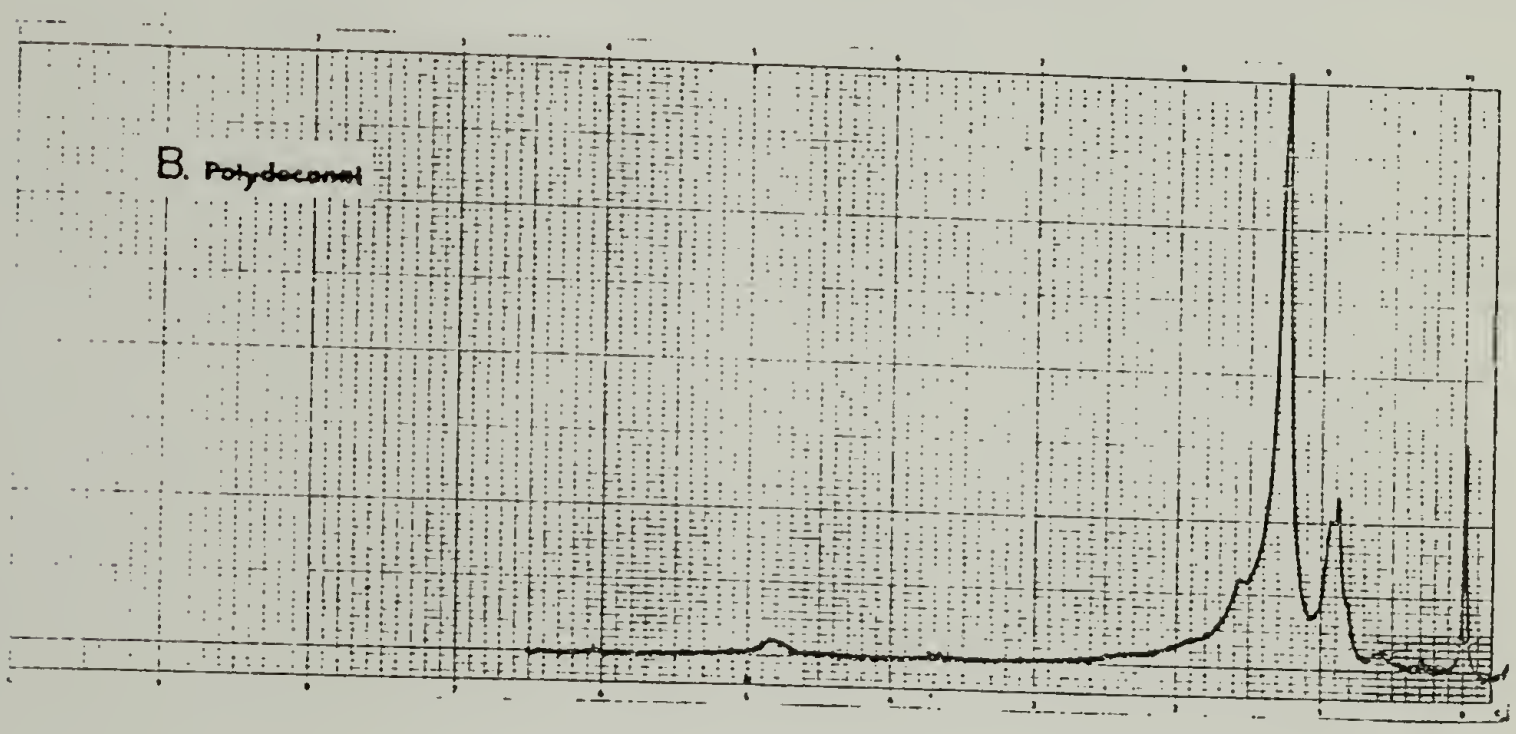
A. Polynonanal

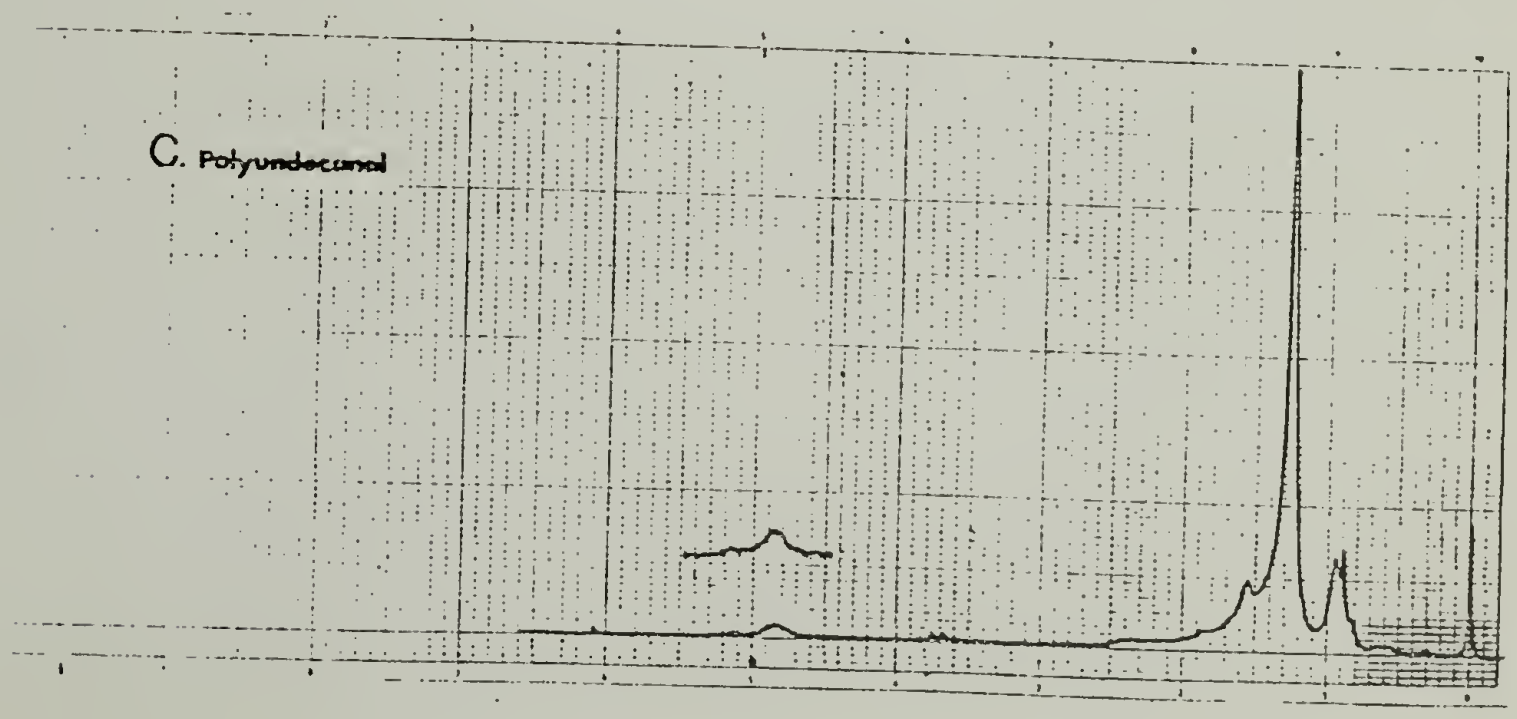


B. Polyundecanal

Figure 10: 90 MHz PMR Spectra of Higher Polyaldehydes







polymer chains (e.g. formation of a helix, etc. in solution) or the higher viscosity of the polymer solution. Although no firm evidence regarding the stereochemistry of PNA-I or PNA-II was obtained from PMR measurements it was believed that both polymers were highly isotactic. The tacticity of PHA, prepared by anionic polymerization, had been investigated by PMR spectrascopy (300 MHz) and the polymer was found to be highly isotactic[21]. Since PNA-I was prepared under essentially the same conditions (solvent, initiator, temperature) as the PHA discussed, it is reasonable to suggest that PNA-I was similarly highly isotactic. The similarity in properties between PNA-II and PNA-I suggested that both samples were the same.

b. Thermal stability of the polymer. The thermal stabilities of PNA-I and PNA-II were investigated by thermogravimetric analysis (TGA). Generally speaking, even well stabilized samples of higher aliphatic polyaldehydes will thermally degrade at temperatures near or above 150°C. Because the boiling points of aliphatic aldehydes increase as the length of the alkyl group is increased the boiling points of the thermal degradation products (principally monomer) of longer side chain polyaldehydes may lie near or even above the temperature at which the rate of degradation of the polymer becomes significant. In this situation, the rate of weight loss of samples of polyaldehydes becomes more sensitive to the rate of volatilization of the thermal degradation products.

The results of TGA of aliphatic polyaldehydes are known to be influenced by a number of factors, the most important of which are the crystallinity of the polymer and, especially, the kind and level of

impurities present in the polymer[77]. In the work reported here the temperature of onset of weight loss and the temperature of a fixed small percent weight loss (5%) were found to give the most reproducible indication of polymer thermal stability as measured by temperature programmed TGA and these data gave the best correlation with other experimental observations. In some cases the results of differential scanning calorimetry (DSC) could also be correlated with polymer stability.

PNA-I and PNA-II were prepared and endcapped by different procedures. The endcapping of PNA-I was carried out under conditions which should have favoured more complete acetate endcapping of the polymer. The thermal degradation of polyaldehydes occurs primarily by an unzipping mechanism which begins at the chain ends. Thus, other factors being held equal, it would be expected that a polymer with more stable endgroups would have a higher thermal stability. Because polymer degradation begins at the chain ends the results of TGA of a sample of polyaldehyde could depend upon the molecular weight of the sample, if a law of mass action applies to the polymer degradation.

PNA-I showed an onset of weight loss (degradation) at 110^{o}C and had a temperature of 5% wt. loss of 115^{o}C when the polymer thermal stability was investigated by TGA at a programmed heating rate of 20^{o}C/min.. The temperature of onset of degradation was 93^{o}C and the temperature of 5% wt. loss was 97^{o}C for acetone treated PNA-II under the same conditions. Both PNA-I and PNA-II had a temperature of maximum rate of weight loss (MDT) near 160^{o}C; there was only a slight difference in shape and general characteristics between the TGA curves of PNA-I and PNA-II. The lower temperature of onset of degradation and

lower temperature of 5% wt. loss recorded for PNA-II as compared to PNA-I was attributed to the lower thermal stability of PNA-II because of less complete endcapping of this sample. The fact that the MDT (temperature at maximum slope of TGA curve) was similar for both PNA-I and PNA-II probably resulted from the complex interaction of the various factors which influence polyaldehyde degradation.

The results of TGA experiments indicated that reprecipitation of PNA-II from toluene resulted in a polymer with improved thermal stability. When reprecipitated PNA-II was investigated by TGA the temperature of onset of weight loss and the temperature of 5% wt. loss were 105^{o}C and 110^{o}C respectively. Apparently the most unstable portion of the polymer had been degraded while the polymer was in solution. In addition, the level of impurities was also decreased. The reprecipitated PNA-II had MDT identical to that of the unreprecipitated polymer. The improvement in polymer thermal stability achieved by reprecipitation was seen by DSC.

The relatively higher stability of PHA-I vs. PHA-II was also noticed in the "shelf-life" of the polymer samples when each was stored in an open container at room temperature in the dark. PHA-II was completely degraded to monomer within 2 weeks whereas PHA-I appeared to be unchanged after a period of several months. The deterioration of PHA-I and PHA-II, as determined by visual inspection, was significantly accelerated when the polymers were exposed to ambient laboratory light which probably resulted from autoxidation phenomena.

d. X-ray diffraction by PNA powder. The number and intensity of diffraction maxima photographically recorded for toluene reprecipitated

PHA-II (pg. 272) as compared to PHA-I (pg. 272) indicated a much lower crystallinity for reprecipitated PHA-II. The quenching effect of the toluene reprecipitation procedure was also indicated by DSC. The calculated d spacings (Bragg equation) and relative intensities corresponding to the diffraction rings of the powder diagrams of PHA-I and PHA-II are listed in Table 6 and Table 7 respectively.

The series of d spacings calculated for the strongest diffraction rings of each powder diagram were quite similar which indicated that the crystal structures present in each sample were alike. The major difference between the two diagrams, besides the obvious factor of intensity, was the greater number of diffraction maxima recorded for PNA-II in the region of 2 less than ca.θ10.5^{o}. The lower angle reflections of long side chain polymers are usually related to the spacings of planes which may be either parallel or perpendicular to the planes in which the side chains lie and which are separated by regions of crystalline side chains[68, 115]. Possible interpretations of the x-ray diagrams in terms of the crystal structure of PNA will be considered later in relation to the diffraction diagrams of oriented samples of PNA.

3. Investigation of the melting behavior of PNA by DSC. The melting behavior of PNA, prepared by two different procedures, was evaluated by DSC. It was also found that certain observations made during the investigation of the melting behavior by DSC could be related to the polymer thermal stability. Heating rates of 10^{o}C/min. or 20^{o}C/min. were normally used in the DSC measurements. These heating rates were very convenient and the results obtained at these heating

TABLE 6

X-ray Diffraction by PNA-I[a]

Reflection #	Relative Intensity	d (in Å)	Comments
1	m	21.15	
2	vs	15.20	sl. diffuse
3	w	12.74	" "
4	w/m	10.48	
5	w	8.12	
6	m/s	7.38	
7	w/m	6.59	
8	w	5.15	
9	s	4.66	
10	w	4.36	
11	s	4.15	diffuse
12	w	3.63	

[a]Acetone washed powder. Exposure time, 6 hrs.; sample-to-film distance, 113mm..

TABLE 7

X-ray Diffraction by PNA-II[a]

Reflection #	Relative Intensity	d (in Å)	Comments
1	s	21.39	sl. diffuse
2	vs	15.30	
3	vw	11.37	
4	m/w	7.68	
5	vw	6.88	
6	m/w	4.86	
7	m/s	4.19	diffuse
8	vw	3.78	
9 (?)	vw		

[a]Polymer reprecipitated from toluene and ground at -50°C. Exposure time, 6 hrs.; sample-to-film distance, 114mm..

rates were the most reproducible. In general, the results obtained at higher heating rates did not differ significantly from those obtained at 10^{o}C/min. or 20^{o}C/min.. When lower heating rates were used it was believed that the DSC scans did not truly reflect the initial properties of the sample. Such a phenomenon is commonly encountered in dynamic thermal experiments such as DSC. It was believed that when lower heating rates (e.g. 2.5^{o}C/min.) were used, polymer degradation and polymer recrystallization (which may be influenced by monomer) both occurred to a significant extent during the experiment. Hence, these effects may have clouded the effects of the desired variables (quench, annealing temperature, etc.) when lower heating rates were used. Unless otherwise noted, the precision of the transition enthalpy measurements was ±3% or better (95% confidence). The peak temperatures measured were believed to be within 3^{o}C of their actual values at the specified heating rate.

Two transition regions were identified by DSC in both samples of PNA, similar to the behavior which had been observed for other, previously known long side chain polyaldehydes[75]. In analogy with other long side chain polyaldehydes, the first melting region of PNA, which was observed between 40^{o} and 70^{o}C, corresponded to changes in structuration of or "melting" of the polymer side chains. The first, or side chain, transition itself appeared as one or more "transitions", in as much as the DSC thermograms of the polymer showed fine structure in this temperature region. The second transition was normally observed in the range of 120^{o}-135^{o}C. This second transition, which was assigned to melting of crystal structures in which the main chain

participated, was characteristically observed as a more or less pronounced shoulder on the broad decomposition endotherm which was usually recorded in the DSC scans of PNA at 160° to 175°C. Because polymer degradation readily occurred at higher temperatures the behavior of PNA in the second transition region could not be investigated in as much detail as in the first melting region. The occurrence of this dual melting behavior in PNA could be verified by optical microscopy using a hot-stage accessory.

Baseline departure and return points, and to some extent endotherm shapes, were found to be dependent upon sample geometry. For this reason peak temperatures were taken to describe the melting behavior and transition temperatures. The peak temperatures were more reproducible and gave better correlation with transition temperatures determined by other methods. It should also be noted that the transition enthalpies were also found to be somewhat dependent upon sample geometry although such variations were rarely more than 6% (twice the precision of the experiment).

Typical DSC scans recorded for PNA-I are shown in Figure 11, those for PNA-II are shown in Figure 12. In Figure 12 only the first transition region is shown, since the DSC scans of PNA-II in the second transition region were identical to those of PNA-I. The pertinent data regarding the DSC thermograms of the Figures is given in Table 8 and Table 9. In some instances, endotherms were recorded below room temperature in the DSC scans of samples of PNA.

The temperature range of the first transition region was very similar for both samples of PNA. However, there was a difference in

Figure 11: DSC of Polynonanal (PNA-I)

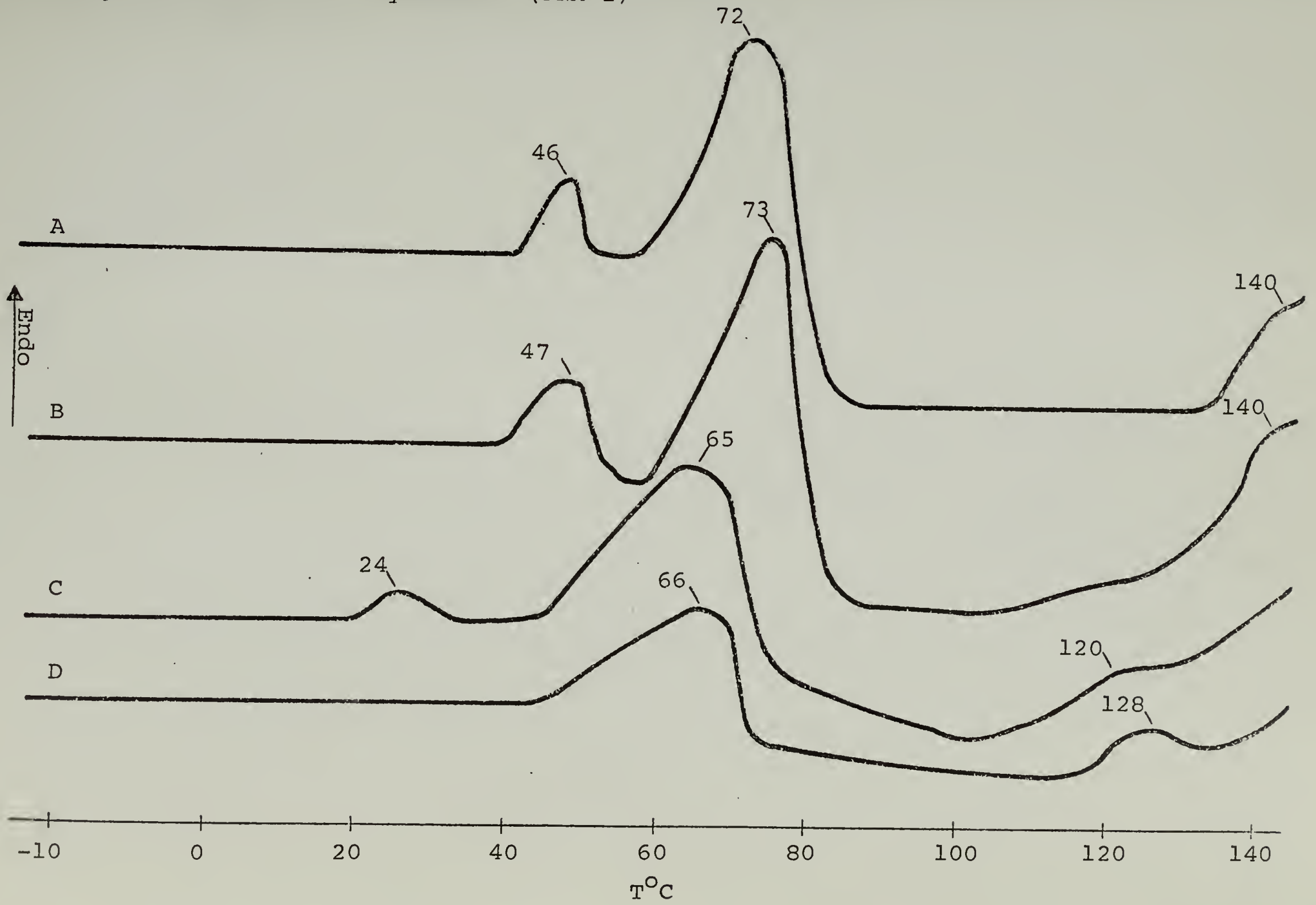


Figure 11: (cont'd)

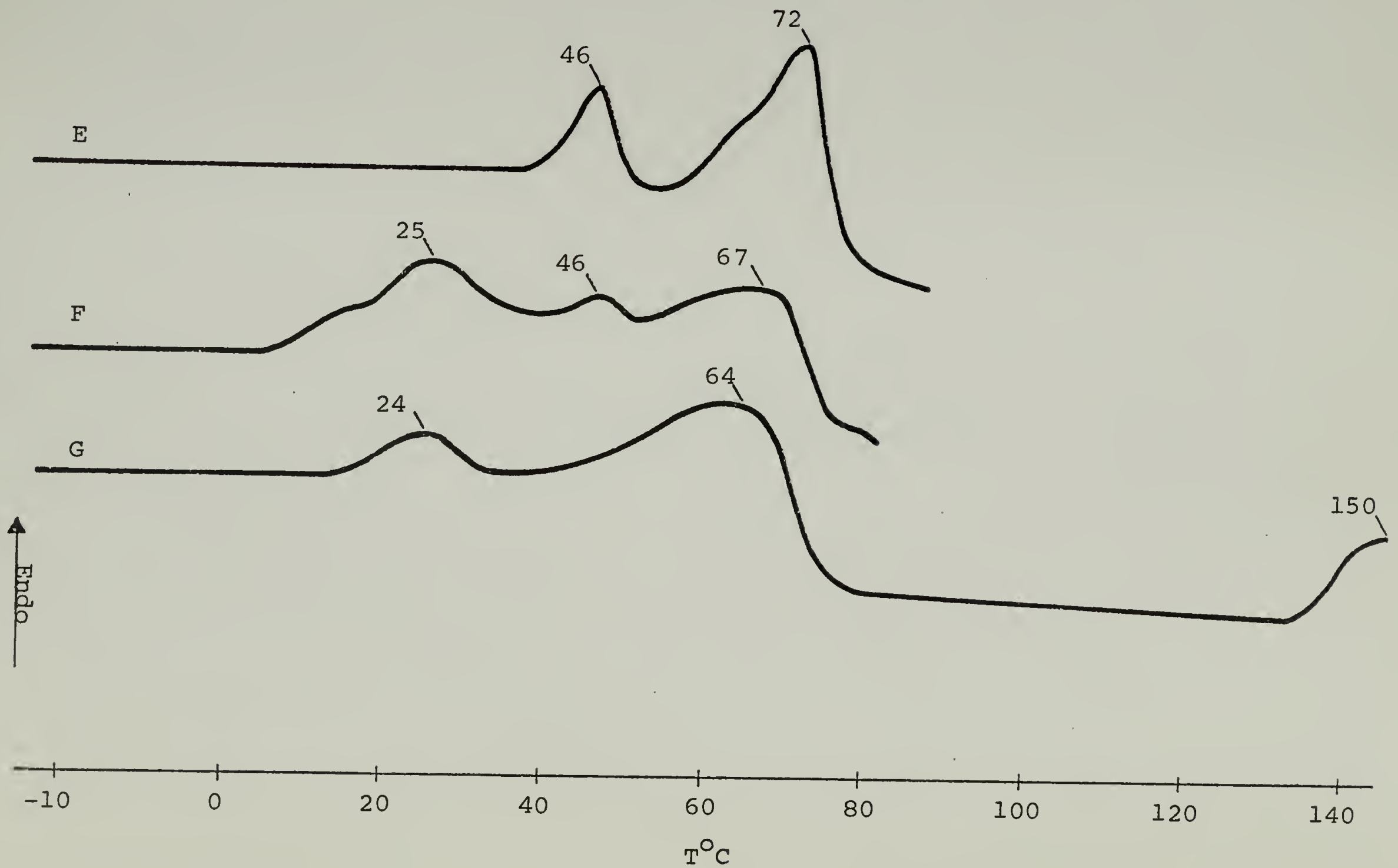


TABLE 8

DSC of PNA-I[a]

Scan[b]	Sample Description	First Transition Peak Temperatures (in °C)	ΔH First Transition (in cal./g.)	Second Transition[c] (in °C)
A	Virgin	46; 72	5.15	-
B	Quenched after first scan, (A), to 85°C	25; 46; 67	5.56	-
C	Following (B), quench to 68°C, anneal 12min., quench	24; 64	5.93	150
D	Heated to 41°C, annealed 12 min., quenched	46; 71	5.37	140
E	Heated to 49°C, annealed 17 min., quenched	47; 73	6.41	140
F	Heated to 72°C, annealed 15 min., quenched	24; 65	6.22	120
G	Heated to 77°C, annealed 15 min., quenched	66	7.19	128

TABLE 8 (cont'd)

[a]Data corresponding to DSC scans of Figure 11; heating rate, 20°C/min..

[b]Same as in Figure 11.

[c]Estimated

Figure 12:

DSC of Polynonanal (PNA-II)
(20°C/min.)

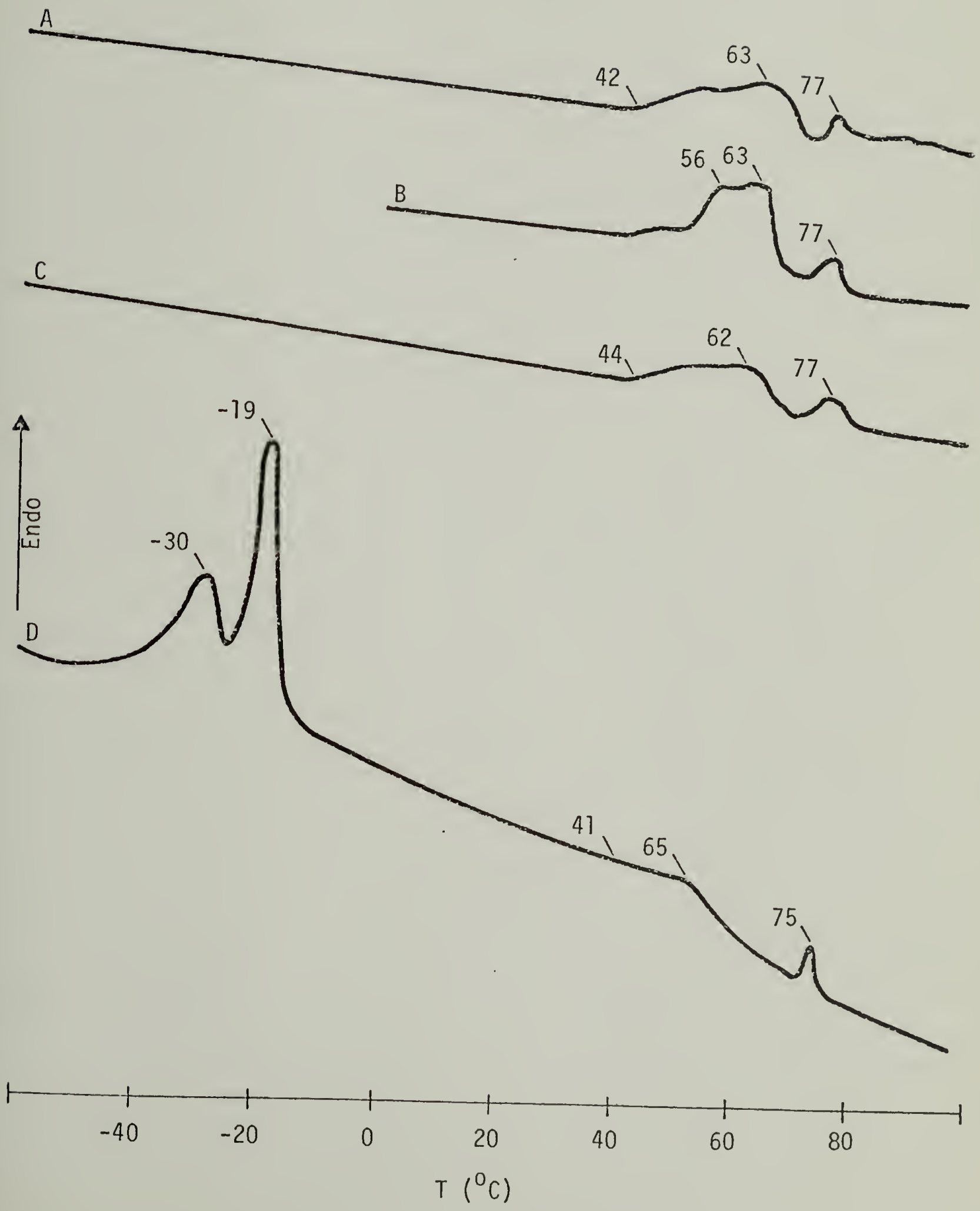


TABLE 9

DSC of PNA-II[a]

Scan[b]	Sample Description	First Transition Peak Temperatures (in ^{o}C)	ΔH First Transition (in cal./g.)	Second Transition[c] (in ^{o}C)
A	Virgin	50, 63; 77	5.3	-
B	After first scan (A) to 95°C, quench to 47°C, anneal 10 min., quench	50, 63; 77	6.6	130
C	Virgin	47, 65; 77	4.9	-
D	After scan (C) to 100°C, quench to 90°C, anneal 10 min., quench	(65; 75)[d]	2.9	(110)

[a]Data corresponding to DSC scans of Figure 12; heating rate, $20^{o}C$/min..

[b]Same as in Figure 12.

[c]Estimate

[d]Low temperature transition recorded with peaks at -30^{o} and $-19^{o}C$. Total area of low temperature transition corresponded to 19 cal./g. based on initial sample weight.

peak temperatures and endotherm fine structure between scans of PNA-I and PNA-II. Furthermore, the enthalpy associated with the first transition of a sample of PNA-I was always lower than that associated with a sample of PNA-II when both samples had been given a similar thermal history in the calorimeter. Such difference between PNA-I and PNA-II probably reflected the different histories imparted to the samples during synthesis, stabilization, and isolation of the polymers. (PNA-I was isolated by direct filtration of the hot endcapping reaction mixture through a warm funnel and cooled to room temperature at a moderate rate. On the other hand, PNA-II was never heated above room temperature and was obtained by filtration of the reaction mixture with the aid of a nonsolvent.) The effect of sample prehistory (i.e. treatment of the sample before calorimetric measurements) upon the behavior of the sample in the first transition region was also observed when a sample of PNA-I was reprecipitated from $CHCl_3$. When a sample of the less $CHCl_3$ soluble PNA-I was scanned to 80^oC a multipeaked endotherm was observed which had a major peak at 46^oC and minor peak at 61^oC; the total heat of fusion in the first transition region was 3.4cal./g.. When the sample was subsequently quenched from 80^oC and rescanned, the endotherms of the first transition region were much broader, the peak temperatures were lower, but the enthalpy associated with the first transition region was increased to 5.0cal./g..

The melting behavior of PNA-II was drastically altered when the polymer was reprecipitated from toluene. Typical DSC scans recorded for reprecipitated PNA-II are shown in Figure 13, the data pertaining to the several curves of Figure 13 are collected in Table 10. As

Figure 13: DSC of Reprecipitated PNA-II

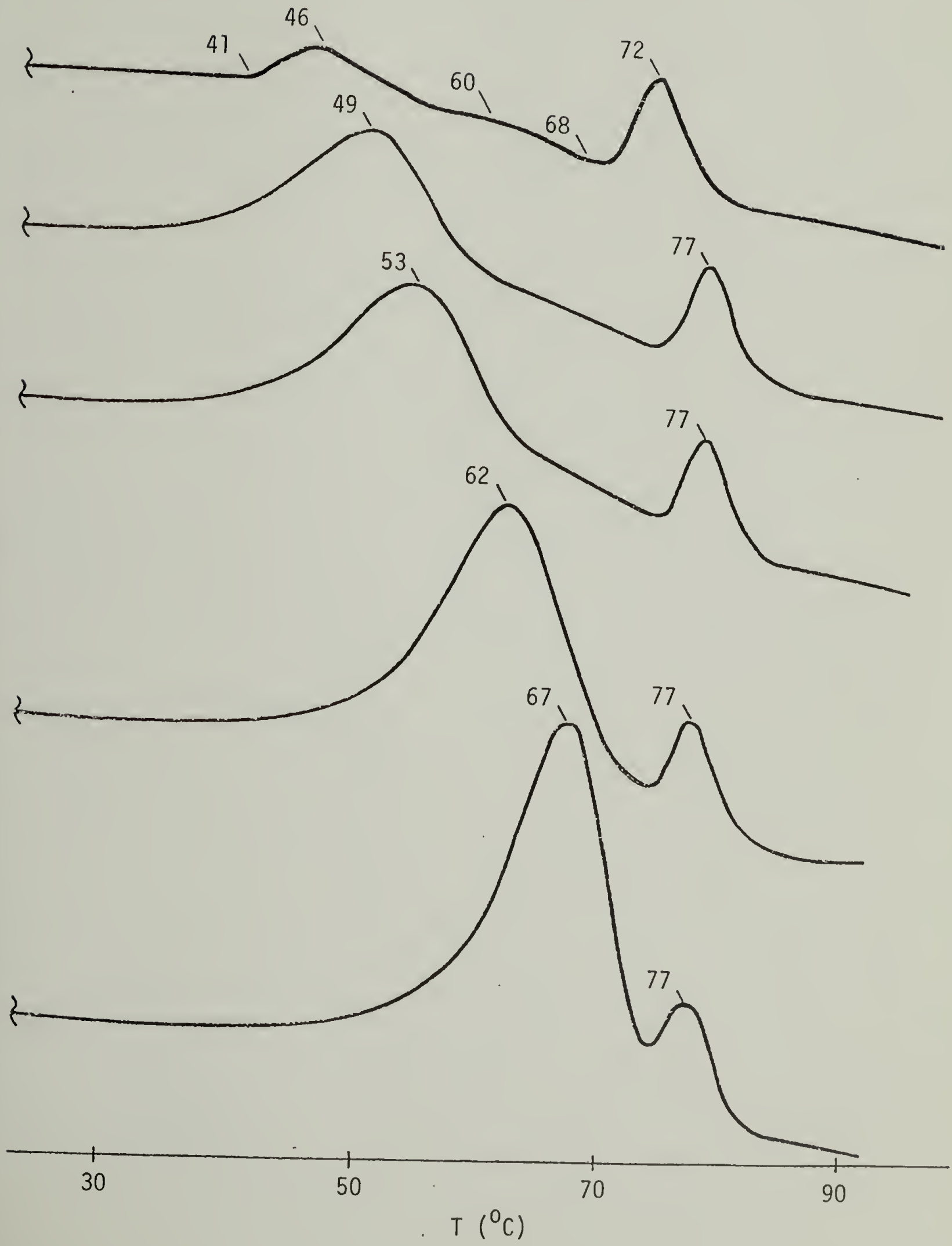


TABLE 10

DSC of PNA-II Reprecipitated from Toluene[a]

Scan[b]	Sample Description	First Transition Peak Temperatures (in ^{o}C)	ΔH First Transition[c] (in cal./g.)
A	Initial scan to 90°C	46; 72	2.1
B	Hold 1 min. at 90°C, quench, scan to 90°C	49; 77	5.2
C	Hold 1 min. at 90°C, quench, scan to 90°C	53; 77	6.0
D	Hold 1 min. at 90°C, quench to 52°C and anneal 20 min., quench and scan to 90°C	62; 77	8.0
E	Hold 1 min. at 90°C, quench to 74°C and anneal 10 min., quench and scan to 190°C	67; 77[d]	13.6

[a]Data corresponding to DSC scans of Figure 13; heating rate, 20°C/min..

[b]Same as in Figure 13.

[c]Peak near 77°C made nearly constant contribution of ca. 1cal./g. to the first transition enthalpy (curves A thru D).

[d]Peak Separation was not possible.

previously mentioned, the x-ray powder diagram of reprecipitated PNA-II suggested an overall lower crystallinity for this sample. As indicated in the Figure and accompanying Table, the transition enthalpy of toluene reprecipitated PNA-II in the region of the first transition was significantly lower than that of the native material. When the reprecipitated PNA-II was scanned to a temperature above the first transition but below the second and then subsequently quenched from this temperature and rescanned, the transition enthalpy in the first melting region was increased. This observation indicated that recrystallization and/or reorganization phenomena probably occurred during the experiment and, at least as far as the first transition is concerned, thermal quenching of the sample was less effective in suppressing the crystallization of the sample than was quenching during the reprecipitation procedure.

The lower crystallinity of the reprecipitated PNA-II and the ability of the sample to recrystallize on heating was more dramatically indicated when the sample was observed at different temperatures between crossed polars. When the reprecipitated material was first viewed between crossed polars at room temperature the entire field of view was completely extinct. If the temperature of the sample was increased to 40^{o}C, then, as the temperature approached 40^{o}C, the transmission of light increased and vivid colors were observed in various regions of the sample. The transmission persisted when the sample was removed from the hot stage, quickly cooled to room temperature, and re-examined.

In order to better assess the effect of the reprecipitation procedure on the properties of the polymer and, hopefully, gain more detailed insight into the nature of the crystallization of the polymer,

it was decided to anneal the toluene reprecipitated PNA-II at a temperature near 100°C, midway between the two transitions of PNA. It was thought that such treatment might result in a material that would have a melting behavior similar to either PNA-I or native PNA-II. However, polymer degradation occurred to a significant degree during such treatment and the effects of degradation complicated the effects of the thermal treatment, thus the results of this experiment were very ambiguous.

In addition to the transitions already discussed, another transition, which occurred below room temperature, was also recorded in some thermograms of PNA (see Fig. 12, curve D). These sub-ambient peaks were most frequently observed in DSC scans of samples of PNA-II which had been heated one or more times to temperatures of 70°C and above. Occasionally, low temperature peaks were recorded in the DSC scans of virgin samples of PNA-II. The DSC scan of a virgin sample of PNA-II, which showed sub-ambient peaks in its initial scan, is reproduced in Figure 14. This sample was the same as that for which the thermograms of Figure 12 were recorded except that the sample was aged in the sealed DSC pan for 36 hrs. before the measurement was made. Peaks occurring below room temperature were not found in the DSC scans of PNA-I. The sub-ambient transition of PNA was spread over a temperature range of as much as 40°C and generally was observed as one or more peaks with shoulders.

It was intriguing to consider the possibility that such sub-ambient transitions, which were previously unreported for long side chain polyaldehydes, were an indication of polymorphism or multiple phase

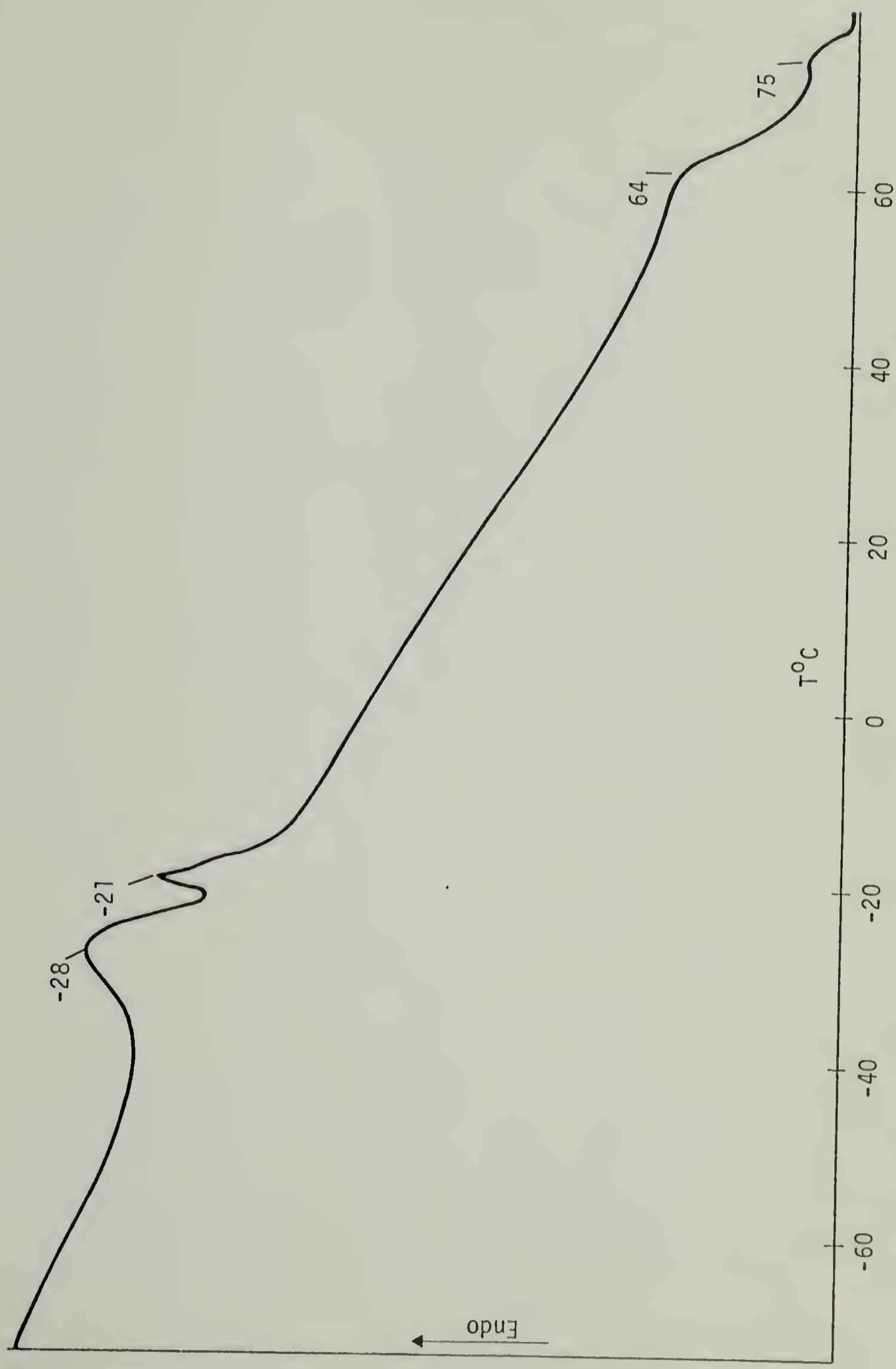


Figure 14: DSC of Polynonanal (PNA-II); Sample Aged in DSC Pan (20°C/min.)

transitions of the alkyl side chains of the polymer. The occurrence of polymorphism in the case of low molecular weight long chain compounds (e.g. triglycerides of fatty acids) is well known[127]. However, polymorphism or multiple phase transitions in relation to the crystallization of the side chains of comb like polymers has never been documented; even in those cases where the corresponding monomers exhibit polymorphism. More careful examination of the thermograms of PNA indicated that the lowest temperature transitions were not manifestations of multiple phase transitions involving solely the polymer side chains. If this were the case, then such behavior would have been strong indication that true "independent" side chain crystallization occurred in PNA.

The consideration of three factors indicated that the sub-ambient peaks in DSC scans of PNA were due to the presence of monomeric nonanal in the samples and not due to the occurrence of multiple phase transitions. Firstly, the temperatures of these peaks, particularly the one at the higher temperature, corresponded quite well to the melting point of monomeric nonanal as determined by DSC. Secondly, there was no straight forward effect of thermal history upon either the low temperature peaks or the first transition peak (40^{o}-70^{o}C) or their relationship. Thirdly, there was no correlation between the sub-ambient peaks and the first transition peaks of the kind which would have suggested polymorphism or multiple phase transition behavior. If indeed the low temperature peaks and the first transition peaks represented the melting of two different crystalline modifications of the aliphatic side chains which could not be interconverted by a reversible process,

then, depending upon thermal history, one transition should have dominated over the other. The only simple and reproducible effect of thermal history upon the relationship of the low temperature and first transition endotherms was that, as the sample was repeatedly scanned to or annealed at temperatures near or above 70°C, then the low temperature endotherms always increased at the expense of the first transition endotherms. If a reversible transformation of one crystal structure to another was responsible for the observations in question, than a discrete relationship between the low temperature transitions and the 40° to 70°C transitions should have existed. If kinetic factors hindered the complete interconversion, then a specific effect of thermal history upon the two sets of endotherms was expected. All these considerations led to the conclusion that the low temperature peaks were most likely the manifestation of the presence in the samples of monomeric nonanal, either initially present or formed in situ by polymer degradation.

The presence of monomer in the polymer affected the crystallization and melting behavior of the polymer in a complicated way, particularly in the first transition region. When monomer was present in the sample, the enthalpy associated with the first transition endotherms (40° to 70°C) was always depressed, except when the level of monomer was very low. The first transition endotherms were always broadened and the peak temperatures were at lower temperatures when monomer was present in the samples. Monomer was compatible with polymer, swelling the polymer at room temperature and dissolving it at temperatures greater than ca. 50°C. It is possible that, at low concentration, monomer

plasticized the polymer and aided its crystallization rather than hindering it. However, transition enthalpies of 3.0cal./g. or less were usually calculated for the first transition endotherms when it was suspected that monomer was present in significant amounts (i.e. if noticeable low temperature peaks were recorded). This effect was true even if the weight of the polymer sample was corrected for loss to degradation by assuming the entire low temperature transition to be monomer and calculating the apparent weight of monomer by using the data of Table 5.

When a low temperature transition was observed in samples this was normally observed as two overlapping peaks; a broad peak near -30°C, whose position was variable, and a sharper peak near -20°C, which frequently had a shoulder on its low temperature side. When this low temperature transition first appeared in a sample, presumably at relatively lower monomer concentration, the relative areas of the two overlapping peaks appeared nearly equal with the -30°C peak perhaps being slightly larger. In comparison, when monomer alone was investigated by DSC under similar conditions, only one peak was observed which most closely resembled the -20°C peak of the low temperature transition. The peak at -20°C became predominant in a polymer sample, which showed sub-ambient transitions, if the sample was subjected to conditions which favored polymer degradation. The -20°C peak clearly dominated at estimated monomer concentrations above ca. 25%. It was also noted that, if significant low temperature peaks were recorded in the initial portion of the thermogram of a sample, then the endotherms in the second transition region (120°C), including the decomposition endotherm,

were significantly smaller or completely absent. This observation was expected if it was assumed that the low temperature peaks were due to monomer which resulted from polymer degradation and which facilitated further polymer degradation by acting to swell or dissolve the polymer.

When low temperature peaks were observed, the details of the DSC scans in this temperature region could not be explained solely on the premise of fusion of monomeric nonanal. Two possible explanations of the details of the sub-ambient peaks were considered; both of which indicated limited miscibility of monomer and polymer at these temperatures. Firstly, it was considered that the two sub-ambient peaks were the result of fusion of monomeric nonanal in two different environments. That is, the peak at -20^{o}C may have resulted from the fusion of "free" monomeric nonanal, which crystallized without influence of the polymer, whereas the peak near -30^{o}C may have represented the fusion of monomeric nonanal which was miscible with the polymer. The second possible explanation considered was that monomer and polymer were capable of cocrystallization and exhibited solid solution, eutectic, or similar behavior. In this event it was thought that the -30^{o}C peak represented the fusion of such cocrystalline regions, probably rich in monomer, while the peak at -20^{o}C represented the fusion of "free" monomer present above the miscibility limits. The results of the direct observation of the melting behavior of PNA by optical microscopy, when the polymer was deliberately contaminated with monomer, were consistent with either explanation and served to verify the general results of DSC investigation. The microscopic experiment did show that only the crystallinity responsible for the first transition of PNA was present in samples

which had been degraded to a significant extent.

4. Extrusion of PNA and characterization of the extrudate. PNA-I and PNA-II, as obtained, were brittle, easily crumbled powders at room temperature. However, when PNA was heated to a temperature which was near or above the upper limit of the first transition region a greater degree of molecular mobility existed in the samples. At such temperatures the polymer could be extruded through an orifice. This behavior is characteristic of other polyaldehydes, possessing sufficiently long side chains, which, like PNA, soften but do not flow when heated above their first transition[77]. X-ray examination of extruded PNA indicated that significant orientation was achieved in the extrusion process, in complete agreement with what had been known from PHA.

When a sample of PNA was extruded at 80°C through a 0.762cm. capillary a smooth trace of the force required to maintain constant crosshead speed was obtained; the value of the apparent viscosity at the steady state was 3350 poise. The slightly opaque filament easily supported its own weight to at least 40cm. below the die and readily coiled before breaking as it was collected. Some of the curvature introduced when the filament was coiled became set as the filament cooled to room temperature. Polymer degradation occurred during the extrusion process as evidenced by the odor of monomer which was detected and by the infrared spectrum of material salvaged from the rheometer.

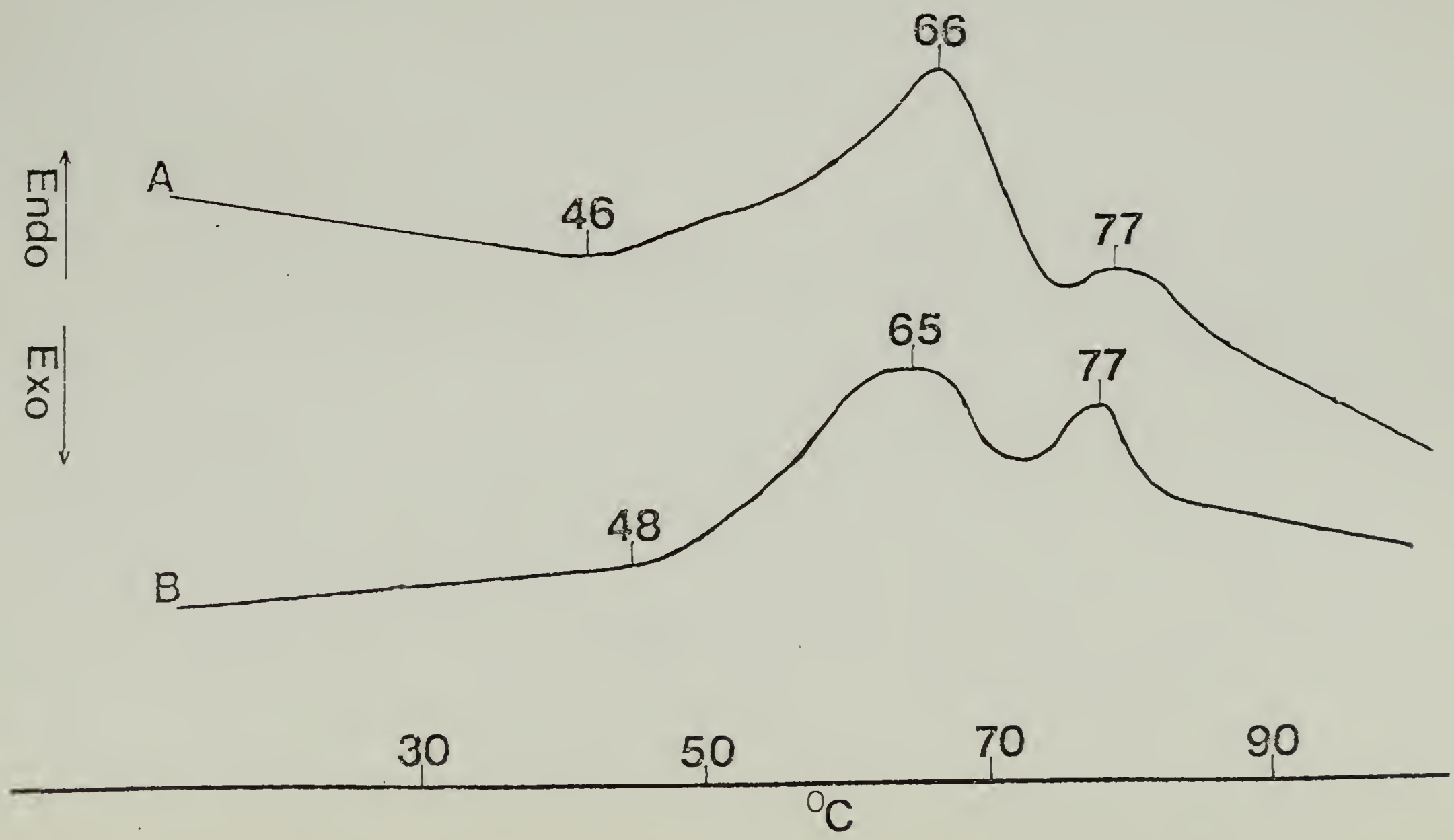
The TGA curve of extruded PNA-II (PNA-IIE) was slightly different than that recorded for the original material; the onset of weight loss was 105°C. The TGA curve appeared as a straight line from 145° to 195°C which represented the portion of the curve of maximum negative slope.

Degradation of less stable fractions during extrusion and, possibly, changes in the crystallinity of the polymer were believed to be the reasons for the slight differences between the TGA curves of extruded and non-extruded PNA.

Two transition regions were observed when the melting behavior of PNA-IIE was investigated by DSC and optical microscopy, the transition regions of the extruded polymer were essentially the same as for the unextruded polymer. The DSC scans of extruded and unextruded PNA are compared in Figure 15, only the first transition region is shown. The enthalpy associated with the first transition endotherms was always lower for the extruded samples than for powdered samples. Typically, values of 4 to 6cal./g. were observed for the first transition of extruded PNA whereas values of 5 to 7cal./g. were recorded for unextruded PNA (except for sample reprecipitated from toluene). As suggested in Fig. 15, the temperature of the major peak of the first transition region was slightly lower for the extruded sample. Furthermore, the enthalpy associated with the first transition of a sample of the extrudate was always greater when the sample was scanned a second time, unless the sample had been scanned to a temperature greater than 95^{o} to 100^{o}C. This increase in transition enthalpy was observed regardless of whether the sample was cooled slowly or rapidly after the first scan; the rate of cooling did, however, affect the peak temperatures. The behavior of PNA-IIE was completely analogous to that which had been observed for extruded PHA excepting that the decrease in peak temperatures and transition enthalpies observed for the extruded samples, as compared to powdered samples, was not as dramatic in the case

Figure 15: DSC of Powder vs. Extruded Polynonanal (PNA-II) (20°C/min.)

A-Powder
B-Extruded



of PNA as in the case of PHA. The thermograms of extruded PNA also differed from those reported for extruded PHA in that the DSC scans of the former showed less distinct fine structure than those of the latter. As previously mentioned, the orientation effect of the extrusion process was the same in the case of PNA as reported for PHA.

The appearance of the DSC scans of PNA-IIE in the second transition region was very similar to that of the DSC scans of PNA powders. However, the baseline departure at the second transition was sharper in the case of extruded samples of PNA than for powdered samples. This observation was believed to reflect differences between the samples in regards to crystallinity, sample geometry, or both.

Two transitions were also observed for PNA-IIE when samples of the extrudate were examined between crossed polars with a hot-stage equipped microscope at a heating rate of $10^{o}C$/min.. Notable changes in the pattern and color of transmitted light occurred between 60^{o} and $68^{o}C$. Only very small changes in the sample were observed as the temperature of the sample was raised to $115^{o}C$ when the sample transformed into an optically isotropic material at 115^{o} to $120^{o}C$. The softness and pliability of the sample at temperatures intermediate between the two transitions was also verified by optical microscopy. When 0 or 1 cover slips were employed, no deformation of the sample was observed until the temperature of the sample had been increased to $115^{o}C$. If, however, several cover slips were used so that the closure of the hot stage exerted a force on the sample, then the sample was seen to deform at temperatures of 75^{o} to $85^{o}C$.

As mentioned earlier, the x-ray diagrams of PNA-IIE indicated that

TABLE 11

X-ray Diffraction Data for Extruded Filament of PNA-II[a]

Reflection #	Relative Intensity	d (in Å)	Tentative Assignment[b]	Comments
1	s	21.13	---	equitorial
2	vs	15.28	200	equitorial
3	m	10.83	220	"
4	vs	7.73	400	"
5	vw	7.43	---	
6	s	6.82	420	equitorial
7	w	5.43	440	"
8	vs	4.87	620	"
9	vw	4.55	---	"
10	s	4.27	640	reflection at this spacing may be visible in meridonal regions
11	w	4.19	---	extends from equator
12	vw	3.80	---	stronger away from equator
13	vw	(3.5)		?

[a]Single filament; exposure time, 8 hrs.; sample-to-film distance, 89mm..

[b]Assuming a model analogous to that suggested for PHA by Wood, Negulescu, and Vogl[77] ; with a=30.56Å.

significant orientation occurred during the extrusion process. The pattern of intensities observed for PNA-IIE (pg. 185) was very similar to that which had been reported for extruded PHA and suggested that the crystal structure of PNA might be similar to that proposed for PHA. In fact, most of the reflections observed in the diffraction diagram of PNA-IIE could be assigned on the basis of a tetragonal unit cell (see Table 11), completely analogous to that proposed for PHA, having $a=30.56\text{Å}$. The c length was not directly determined but was believed to be the same as in PHA, namely $c=4.52\text{Å}$. Several diffraction rings were observed which were not assigned on the basis of the tetragonal unit cell, similar to what had been reported in the case of PHA. The reasonable agreement between the observed and predicted d spacings strongly suggested that PNA, like PHA, is capable of crystallizing in a manner whereby both main and side chains participate in the unit cell of the crystal lattice.

5. Melting behavior and crystal structure of PNA. Two transition regions were evident in samples of PNA when the melting behavior of the polymer was investigated by DSC and optical microscopy. X-ray diffraction measurements, particularly with oriented samples, performed at room temperature strongly suggested that PNA was capable of existing in a crystalline form in which both main chains and side chains participate in the unit cell. When this is the case the unit cell is most likely tetragonal having 4 polymer chains, in a 4/1 helical conformation, per unit cell in which the sense of the chain helices alternate within the unit cell. This crystal structure was suggested for PNA on the basis of the crystal structure of PHA. The proposed unit cell of

PHA, and PNA as well, was seen to be very similar to the unit cells of polybutanal (PBA) and other polyaldehydes with short side chains. The principal difference between the unit cell of PNA (or PHA) and that of PBA seemed to be the angle of inclination of the side chains with respect to the edges of the unit cell. It appeared that the helices of the long side chain polymers are rotated about their axes with respect to the helices of PBA in order that more efficient packing of the side chains might occur[68].

The strongest diffraction rings observed for oriented filaments of PNA were also clearly observed in the diffraction patterns of powdered samples of PNA. This observation indicated that the same crystal structure was present in all samples of PNA investigated. Although the details of the DSC scans of the various samples of PNA were different, the similarities in the temperature regions of the transitions of the various samples of PNA also suggested that the same crystal structures were present in the samples.

Insufficient data was obtained to allow firm conclusions to be drawn regarding the precise structural changes which accompanied the endothermic transitions of the samples. However, comparison of the results of DSC and x-ray investigation of the melting behavior and crystal structure of PNA against the known behavior of other comb like polymers allowed the range of plausible explanations of the data to be narrowed. It was believed that two types of crystallinity were possible for PNA, the crystallinity being controlled by the side chains when only the outer paraffinic methylene groups entered the crystal lattice. The second type of crystallization thought to be possible for PNA was

one in which both main chains and side chains participated in the crystal lattice, as previously discussed. Both types of crystallinity probably coexisted in samples of PNA. The simultaneous coexistence of both types of crystallinity had been postulated for the case of comb like poly(α-olefins). Polymorphism of crystal structures (or substructures) was also considered as a possible alternative explanation of the dual crystallinity explanation.

Information regarding the packing of the side chains of crystalline PNA was afforded by the infrared spectrum of the polymer in certain frequency regions. However, it was believed that the infrared spectra did not discriminate between side chains packed in "sub-cells" of a tetragonal unit cell and those packed in regions of true side chain crystallization. Indeed, in the case of low molecular weight long chain compounds and several classes of comb like polymers, a correlation had been observed between the mode of packing of the alkyl groups and the infrared spectrum of the compound in the region of $720cm.^{-1}$. In general, a single band of moderate intensity, was recorded near $730cm.^{-1}$ in the infrared spectrum of films of PNA, this absorption always had a noticeable shoulder near $750cm.^{-1}$. If hexagonal packing of the aliphatic side chains predominated, then a single absorption near $720cm.^{-1}$ was expected[128]. A small shoulder on this CH_2 rocking band had been observed when hexagonal packing of alkyl groups was indicated in the case of certain low molecular weight long chain compounds and PHA. Thus, the appearance of the infrared absorption spectrum of PHA in the region of $720cm.^{-1}$ was taken to indicate that the n-octyl side chains of PNA were essentially hexagonally packed. If the side chains

were packed in rhombic fashion, then a doublet should have been observed in the region of 720cm.$^{-1}$.

Since the infrared spectra of samples of PNA were recorded for films of the polymer cast from $CHCl_3$ solution there was some legitimate question as to how well these film data could be correlated with the structure present in other dissimilarly treated samples of PNA. The DSC thermogram in the first transition region of a film of PNA, cast from $CHCl_3$, was qualitatively the same as that of the starting material; suitable allowance being made for the effect of sample geometry. On the basis of this observation it was thought that the infrared spectrum of the film was a fair representation of the sample in general.

The interpretation of the x-ray diffraction diagrams of PNA in terms of a unit cell in which both main chains and side chains participate has already been discussed. The x-ray diffraction diagrams of several samples of PNA indicated that this type of unit cell was present in samples which had significantly different histories. In addition to reflections assignable to this type of crystallization, several reflections were observed which were not readily assigned on the basis of the tetragonal unit cell. The strongest of these unassigned reflections and the one which was characteristically present in all samples of PNA was the reflection which corresponded to a spacing of ca. 4.2Å. Other unassigned reflections were weaker and more or less specific to a sample of PNA which had been treated in a particular way (e.g. extruded, reprecipitated, etc.). Several possible explanations for these unassigned reflections were considered. First, it was thought that these reflections might have been due to the

existence of slight modifications of the tetragonal unit cell, perhaps orthorhombic, in which both main chains and side chains participated. Such a speculation had been offered to account for unassigned reflections and other peculiarities in the case of PHA. A principal drawback to this explanation was that the spacings corresponding to several of the unassigned reflections varied according to the history of the sample of PNA, which would have meant that several modifications of the tetragonal unit cell were possible. If this were the case it was thought that a different one of these should have predominated in at least one of the samples compared to the others. Reflections of different subcells of the alkyl chains within essentially the same tetragonal unit cell was also considered as an explanation for the unassigned reflections.

The third possible explanation of the unassigned reflections that was considered was that these reflections had their origin in a crystal lattice which involved only aliphatic side chains of the polymer. A strong reflection corresponding to a spacing of 4.2Å had been reported in the case of most other types of comb like polymers in which the crystallinity of the polymers was exclusively due to crystallization of the $-CH_2-$ containing side chains which pack in a hexagonal manner. The comparatively diffuse appearance of the 4.2Å reflection of PNA, as well as the fact that this reflection extended from the equator to some extent in oriented samples of PNA, was better reconciled with this third explanation. However, the 4.2Å reflection probably had some contribution from the packing of side chains within the tetragonal unit cell. If most of the unassigned reflections of various samples of PNA

were indeed the result of true side chain crystallization then it was thought that the slight differences in side chain crystallization indicated by x-ray might also be reflected in that portion of the DSC thermograms of the polymers which corresponded to melting of the side chains. In fact a difference in the DSC scans in the first transition region was observed between the various samples which had slightly different unassigned x-ray reflections. That is, the unassigned reflections of PNA were related to the first transition. The differences in x-ray pattern and first transition endotherms was due to variation in packing of the side chains.

The highest transition enthalpies associated with the first transition of PNA were recorded for thermally treated (annealed) samples of the polymer which had been reprecipitated from toluene. Crystallization of side chains of comb like polymers, without incorporation of the main chain, is never truly "independent" of the main chain. The effect of alleviating main chain restrictions on side chain crystallization in the case of vinyl type comb like polymers has been investigated[78]. In the case of PNA various experimental observations indicated that the overall crystallinity in PNA was lowered by the toluene reprecipitation procedure. In this event, the number of main chain units involved in crystallization was lower and the constraints imposed upon those main chain units which do not participate in crystallization was less than in samples with higher main chain crystallization. Thus, when the sample was thermally treated, the side chains attached to non-crystallized main chain units were better able to pack efficiently because of the reduced constraints placed upon them and the heats of fusion were

increased.

The results of experiments conducted with oriented samples of PNA could also be reconciled with idea of true side chain crystallization in PNA. The reduction of transition enthalpy and peak temperature observed for the first transition when PNA was extruded was believed to be due to the disruption of side chain packing imposed by orientation and crystallization of main chain repeat units. Overall, the extrusion process had a less drastic effect on the details of the first transition in the case of PNA than had been observed for PHA. This situation was not totally unexpected since the side chains of PNA are longer and could be expected to exert greater influence on the polymer crystallization than in the case of PHA. In the case of PNA much less drastic thermal treatment was required in order to reverse the effects of the extrusion process on the first transition than were required in the case of PHA.

The one or more peaks observed in the first transition region of PNA were thought to represent slight variations of side chain packing, and perhaps size and perfection of side chain crystallites, which may have been more significant in the polyaldehydes because of the shorter side chain length and difference in polarity between the main and side chain.

E. Polydecanal (PDA)

1. Introduction. Two techniques were successfully used for the preparative synthesis of polydecanal (PDA). In both cases MCH was used as the solvent and LTB was the initiator. One technique was very

similar to the technique which was found to be useful for the preparation of PHA and which was also effective for the preparation of PNA. The second technique involved more careful control of the charging and polymerization temperature, similar to the improved technique for the polymerization of nonanal. In both instances the endcapping reaction was carried out at or below room temperature.

The products obtained by both procedures had the same polyacetal structure. PDA was obtained in higher yield and with higher inherent viscosity when the second technique was used. The purity and concentration of reagents and the temperature history of the polymerization reaction required more careful control to ensure successful polymerization of decanal. When the endcapping reaction was carried out at or below room temperature, the yield of isolated polymer was less sensitive to the time of the capping reaction provided that the duration of the endcapping reaction was less than 4 hrs.. PDA was sufficiently stable so that the polymer could be isolated and handled at room temperature and stored for 2-3 days.

Two transition regions were identified for PDA. At temperatures within the first transition region PDA possessed sufficient mobility so that the polymer could be extruded through an orifice. The extrusion was accomplished under various conditions and with samples of PDA having different histories. The effects of the extrusion process on the melting behavior of PDA in the first transition region were different in comparison to the effects which were found in the case of PNA. X-ray investigations indicated that the orientation induced in the extrusion of PDA was less than that induced in the extrusion of PNA (or PHA).

Attempts were made to prepare oriented specimens of PDA by mechanical treatment of the extrudate. All these attempts were unsuccessful.

2. Synthesis and Characterization of PDA.

a. Synthesis and chemical characterization. PDA was prepared by the anionic polymerization of decanal with LTB in MCH using two different techniques. In the first technique, which was very similar to the technique which had been successful for the polymerization of heptanal and octanal, monomer was injected into a mixture of solvent and initiator which was maintained at -58^{o}C. Decanal is less soluble in MCH than nonanal (or, especially, heptanal) and a significant amount of decanal precipitated immediately when the monomer was injected. However, a sufficient amount of decanal was soluble or dissolved in the polymerization mixture so that polymerization did proceed. (If the initial charging temperature was lower than -58^{o}C when a similar ratio of monomer to solvent was used, then only a trace amount of PDA was obtained.) After a period of 30 min. no changes in the appearance of the polymerization mixture were observed and the polymerization was allowed to proceed overnight at -78^{o}C. A chilled mixture of acetic anhydride and pyridine was added to the polymerization mixture to quench the polymerization and endcap the polymer. The reaction was subsequently allowed to proceed for 1 hr. at room temperature. PDA was isolated by pouring the reaction mixture into chilled methanol and filtering the resulting suspension. PDA with an inherent viscosity of 0.84dl./g. was isolated in 17% yield by this procedure.

In the second procedure monomer was added to a mixture of solvent and initiator which was maintained at -20^{o}C. The temperature of the

polymerization mixture was then brought to -78°C in 1.5 hrs. in a controlled way. After the polymerization mixture was allowed to sit overnight at -78°C a chilled mixture of acetic anhydride and pyridine was added to the polymerization mixture to quench the polymerization and endcap the polymer. The endcapping reaction was subsequently allowed to proceed for several hours at room temperature. PDA with an inherent viscosity of 1.15dl./g. was isolated in 53% yield by pouring the reaction mixture into cold acetone and filtering the resulting suspension. When the reaction mixtures were poured into either methanol or acetone the product was obtained with much greater ease than was PNA when the latter was isolated by direct filtration of the reaction mixture.

Decanal had previously resisted all attempts at its anionic polymerization by conventional aldehyde polymerization techniques. The crystallization of the monomer in the reaction mixture at the polymerization temperature had been cited as the most likely general reason for the failure of these reported polymerization attempts[25]. However, it was found, as discussed here, that with the proper choice of solvent and monomer concentration and with the proper control of temperature, a favorable ratio of the rate of polymerization to the rate of monomer crystallization could be achieved and PDA was obtained. It was also observed that PDA was quite unstable under the conditions traditionally used for the endcapping of polyaldehydes and excessive heating of the endcapping reaction above room temperature drastically reduced polymer yield.

In both procedures the endcapping reaction was carried out only

at room temperature for a period of time. Even when the endcapping reaction was carried out under mild conditions, the polymers were sufficiently stable to be isolated at room temperature and stored for several days. When the endcapping reaction was carried out at room temperature for 1 hrs. (first procedure), the resulting polymer deteriorated (visually) more rapidly than if the endcapping reaction was carried out for a longer period of time (second procedure). PDA obtained by the second procedure, in which the temperature history was more carefully controlled and the endcapping reaction was of longer duration, was used for the characterization of PDA by thermal and other techniques.

The swelling and solubility behavior of higher aliphatic polyaldehydes was considered in discussion of PNA. The solubility characteristics of PDA were the same as those of PNA and PDA could also be conveniently reprecipitated from toluene.

PDA was degraded by 2,4-dinitrophenylhydrazine reagent, the hydrazone melted at 103^{o} to $105^{o}C$. The infrared spectrum of PDA (pg. 259) indicated that the polymer indeed had the expected polyacetal structure. Only minor differences were observed between the infrared spectrum of PDA and that of PNA.

The PMR spectrum of the polymer was also consistent with the structure of the polymer (pg. 268). It was necessary to use a solution of minimal concentration for the PMR experiments because of the viscosity of $CDCl_3$ solutions of PDA. Under these conditions only a weak, broad signal was recorded in the region of δ=4.5-5.0. The presence of some monomer in the sample used to obtain the spectrum was also indicated.

The PMR (90 MHz) spectrum of PDA is shown in Figure 10. The spectrum was very similar to that of PNA. As expected, the apparent relative intensity of the absorption in the region of $\delta 4.8$ was weaker in the case of PDA because of the relatively lower number of acetalic protons. The PMR spectrum of PDA was very similar to that of decanal cyclic trimer and indicated again the similarity in chemical structure between the two species.

b. Thermal stability of the polymer. As in the case of PNA, the temperatures of onset of weight loss and the temperature of 5% wt. loss were found to be the most consistent and reproducible criteria for comparing the thermal stabilities of samples of PDA. Acetone treated PDA had a temperature of onset of weight loss (degradation) of 95°C and a temperature of 5% wt. loss of 105°C. These temperatures were slightly higher than the corresponding temperatures of similarly treated PNA. This situation could have been due to a slightly higher thermal stability of PDA but may simply have reflected the higher boiling point of the thermal degradation products of PDA. When PDA was reprecipitated from toluene the temperatures of onset of weight loss and 5% wt. loss were found to increase indicating a higher thermal stability for the reprecipitated material. This phenomenon, which was also encountered in the case of PNA, was believed to be the result of a decrease in level of impurities in the polymer and the removal of less stable fractions.

The relative stabilities of samples of PDA could also be assessed by visually comparing the shelf life of the samples. PDA which was treated with acetic anhydride for only 1 hr. at room temperature com-

pletely decomposed to monomer (identified as its 2,4-dinitropheynl-hydrazone) within 2 days at room temperature in the dark. A period of 4 to 5 days was required for complete decomposition of PDA which was treated with acetic anhydride for a longer time. When samples of PDA were stored in open containers at room temperature and exposed to ambient laboratory light all samples appeared to deteriorate at a greater rate.

c. X-ray diffraction by PDA powder. The x-ray diffraction diagram of a powdered sample of toluene reprecipitated PDA is shown on page 273, the calculated d spacings and relative intensities are listed in Table 12. The x-ray diffraction diagram indicated that, as in the case of PNA, the overall crystallinity of toluene reprecipitated polymer was lower than in other dissimilarly treated samples. In the case of toluene reprecipitated PDA the strongest diffractions were recorded at smaller angles, in analogy to toluene reprecipitated PNA. In the case of other crystalline comb like polymers, where only the paraffinic side chains participate in the crystal lattice, the small angle x-ray reflections of the polymers had been related to planes which contain the side chain ends and which are perpendicular to the long axis of the side chains. The x-ray diffraction by PDA will be discussed further in relation to extruded samples of PDA.

3. Investigation of the melting behavior of PDA by DSC. The melting behavior of PDA was investigated by DSC. The DSC investigation of the melting behavior of PDA was augmented by investigation of the polymer transitions by optical microscopy. In some cases the observations made during the DSC experiments could be correlated with the

TABLE 12

X-ray Diffraction by PDA[a]

Reflection #	Relative Intensity	d (in Å)	Comments
1	ms	24.28	
2	s	14.41	diffuse
3	m	7.15	near end of diffuse halo
4	m	4.87	
5	m	4.49	diffuse
6	-	-	may be part of diffuse refl.5

[a]Sample reprecipitated from toluene and ground at -50°C; exposure time, 8 hrs.; sample-to-film distance, 114mm.

and thus, polymer degradation effectively overlapped the second transition. As a result of this the second transition and degradation endotherms were usually poorly resolved in DSC experiments. Typically, the second transition of PDA was, at best, observed as an inflection on the low temperature side of the decomposition endotherm. In rare cases a more clearly resolved shoulder, not observed in TGA measurements, was recorded on the decomposition peak. The significant overlapping of degradation with the second transition of PDA was also indicated in hot stage optical microscopy experiments.

Typical DSC scans of different samples of PDA are reproduced in Figure 16, in most cases only the first transition region is shown. Pertinent data relating to the thermograms of Figure 16 are collected in Table 13. In some cases, transitions were observed in samples of PDA at sub-ambient temperatures.

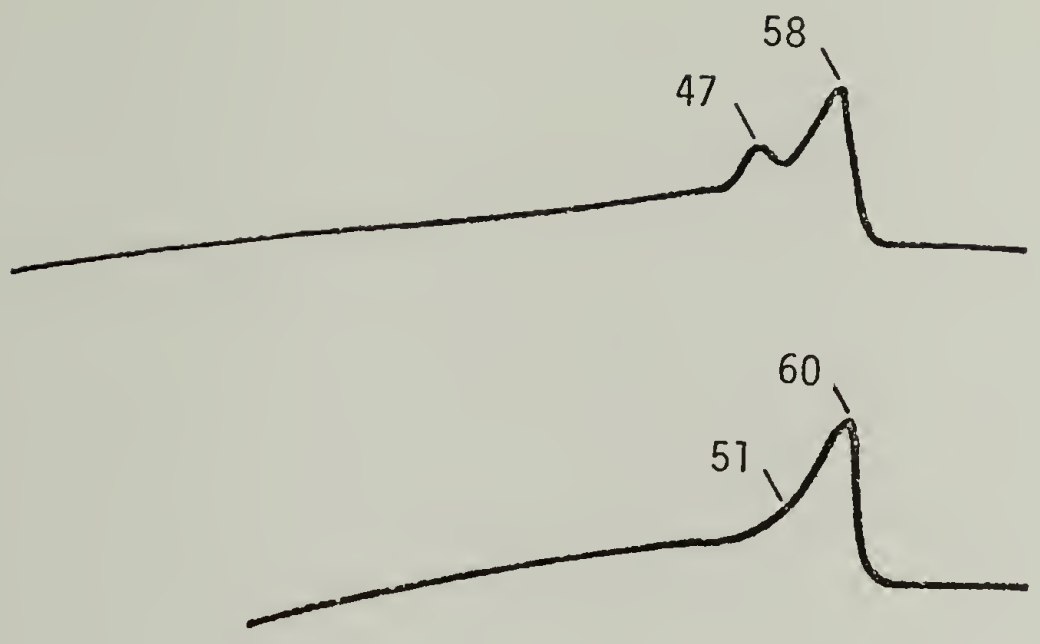
The first transition of powdered samples of PDA showed as two overlapping endothermic peaks or a single peak with very noticeable shoulders. Typically, a transition enthalpy of 10-11cal./g. was observed for the first transition of acetone washed PDA. The details of the first transition of PDA were also sensitive to the treatment of the sample before the calorimetric experiment. This was particularly evident when samples of PDA which had been reprecipitated from toluene were examined by DSC. The enthalpy associated with the first transition of reprecipitated PDA was notably lower than the enthalpy associated with the first transition of the native material (5cal./g. vs. 10cal./g.). The enthalpy always increased when a sample of reprecipitated PDA was scanned through the first transition a second time; this

polymer stability. The instrumental parameters normally used for the investigation of PDA were the same as those normally used in the case of PNA for the same reasons as were previously discussed. Polymer degradation during the DSC measurements was a still more significant factor in the investigation of the melting behavior of PDA than even in the case of less completely stabilized PNA. Unless otherwise noted the precision of the transition enthalpy determinations and the accuracy of the temperature calibration were the same as in the case of PNA. Normally, peak temperatures were found to give the most convenient and reproducible description of the endothermic transitions, particularly in the first transition region.

Two transition regions were observed when the melting behavior of PDA was investigated by DSC. In this respect the behavior of PDA was the same as other higher aliphatic polyaldehydes. The first transition for PDA occurred over the range of 40^{o} to $65^{o}C$ according to DSC and the first transition of PDA was recorded as a series of endothermic peaks or a single peak with shoulders. A transition in this temperature region was also indicated by optical microscope experiments. That is, significant changes occurred in the way polarized light was transmitted through a sample of PDA in the region of 56^{o}-$65^{o}C$, however, the sample maintained a significant degree of structural integrity at these temperatures. A second transition was observed in the region of 110^{o}-$130^{o}C$ by DSC for samples of PDA. When a sample of PDA was observed between crossed polars, the sample transformed to a viscous, optically isotropic fluid at 95^{o}-$110^{o}C$.

Significant degradation occurred in PDA at temperatures near $90^{o}C$

Figure 16: DSC of Polydecanal (PDA)



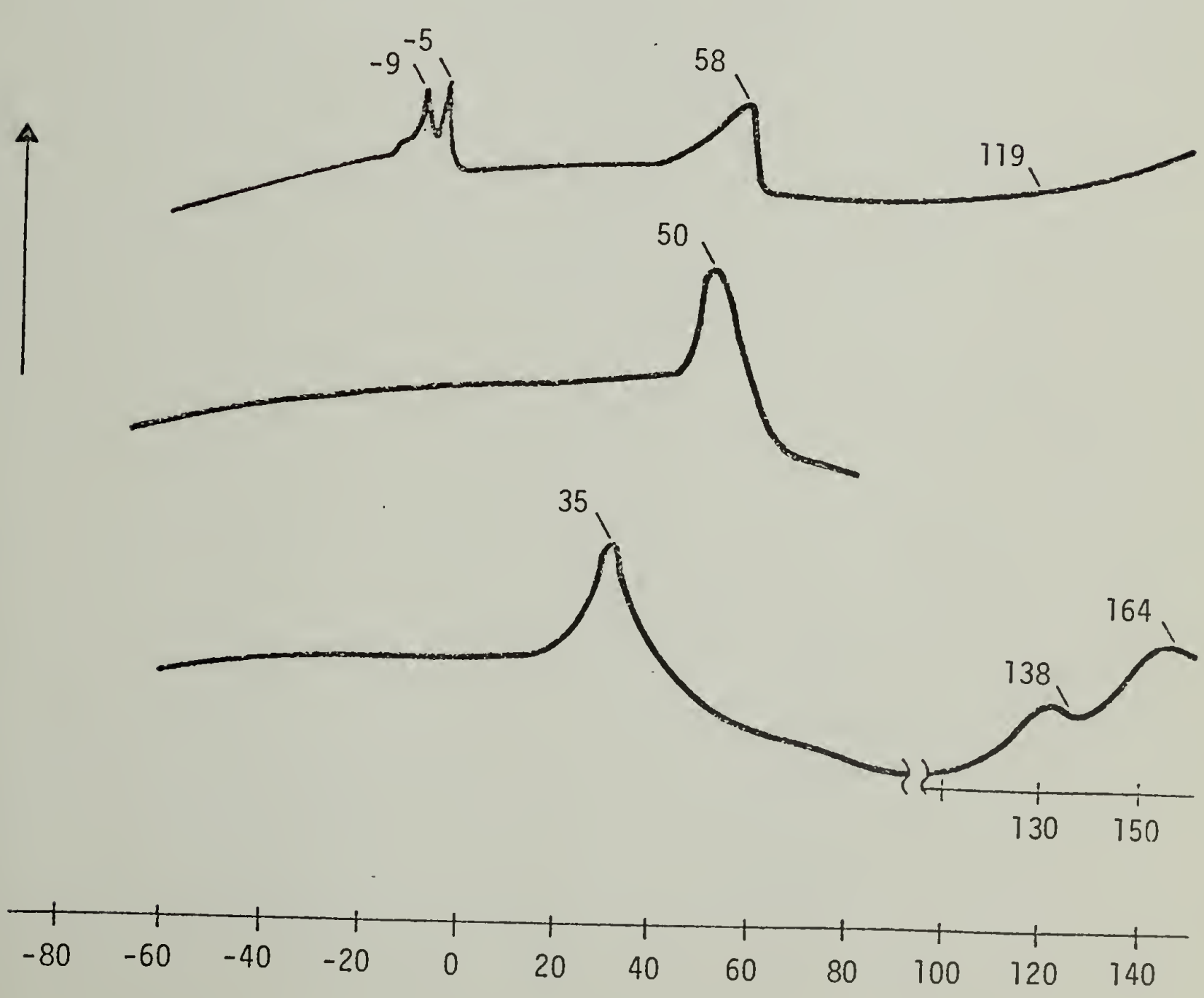


TABLE 13

DSC of PDA[a]

Scan[b]	Sample Description	First Transition Peak Temperatures (in °C)	ΔH First Transition (in cal./g.)	Second Transition[c] (in °C)
A	Acetone treated polymer, first scan to 90°C	47; 58	11.2	-
B	After first scan (A) quench to -30°C and rescan to 90°C	(50)[d]; 60	9.3	-
C	After second scan (B) quench to 57°C and anneal 10 min., quench and rescan	(54)[d]; 58	8.2[e]	(125)
D	Polymer reprecipitated from toluene, first scan to 80°C	50	5.9	-
E	After first scan (D) quench and rescan	35	8.1	(130)

TABLE 13 (cont'd)

[a]Data of DSC scans of Figure 16.

[b]Same as in Figure 16.

[c]Estimated.

[d]Shoulder.

[e]Low temperature transitions recorded, peaks at -9° and -5°C. Area of low temperature transition corresponded to 4.9cal./g. based on initial sample weight.

was true regardless of whether the sample was quenched or cooled more slowly after the first scan. In both these respects the behavior of PDA was very similar to that of PNA and the quenching effect of toluene reprecipitation was indicated also in the case of PDA. The lowering of first transition peak temperatures observed when PDA was reprecipitated was less than that observed in the case of PNA. Furthermore when a sample of reprecipitated PDA was scanned through the first transition region, quenched, then rescanned, the peak temperatures in the second scan were more than 15^{o}C lower although the enthalpy associated with the first transition was nearly 30% higher; this behavior was contrary to that observed for PNA (compare curves D and E of Figure 16 with curves A and B of Figure 13). Reprecipitated PDA was less thermally stable than reprecipitated PNA and, hence, could not be as extensively annealed. However, a trend to increased transition enthalpy with thermal treatment was seen for reprecipitated PDA which, taken with other factors, indicated that toluene reprecipitation produced quenching effects in both PDA and PNA.

The effects of crystallization of side chains in reprecipitated PDA when a sample of the polymer was heated were also seen by optical microscopy as in the case of PNA. The initially high extinction of reprecipitated PDA decreased when the sample was heated to 55^{o}C and the increased transmission persisted if the sample was then cooled.

A transition was frequently seen at below room temperatures in DSC scans of samples of PDA which was believed to be the result of the presence of monomer in the polymer. These low temperature peaks were usually observed in samples of PDA which had been heated or aged in the

DSC sample pans. In general, low temperature transitions were seen in DSC scans of PDA when the sample had been subjected to less drastic conditions than those which resulted in appearance of low temperature transitions for PNA. Normally, this low temperature transition was observed as a multiple peaked endothermic transition. In rare cases, if the relative amount of monomer was assumed to be extreme (high or low) the low temperature transition in PDA appeared more as a single peak.

When low temperature peaks were observed then the details of the first transition of PDA were altered in a complicated way. Generally, if a small (ca. 3cal./g. polymer sample), multiple peaked, low temperature transition was recorded in the DSC scan of a sample, the enthalpy associated with the first transition endotherm was lower in relation to that observed when no low temperature transitions were found. In rare cases if a very small single low temperature peak was recorded in the initial thermogram of a sample, then the enthalpy associated with the first transition closely resembled that observed when no low temperature transitions were recorded (ca. 10cal./g.). If a sample which showed such behavior was heated to ca. 80^{o}C, quenched, then rescanned, then a multiple peaked low temperature transition was recorded and the enthalpy associated with the first transition was depressed. When the sub-ambient peaks were relatively small (corresponding to up to 8cal./g. polymer sample) the relative areas of the low temperature peaks were comparable and enthalpies of up to 6cal./g. were observed for the first transition. As the total area of the low temperature transitions increased, the peaks gradually coalesced to a single peak at -4^{o} to -5^{o}C

which increased at the expense of all other peaks upon continued thermal treatment of the sample.

As the sample was treated in the calorimeter under conditions which were expected to enhance polymer degradation, then the appearance of the low temperature transitions in the "polymer" sample gradually approached that of the DSC scans recorded for monomeric decanal in independent experiments. If a significant low temperature transition was observed, then the transitions normally observed above 90°C (including polymer degradation) were suppressed or totally absent.

The best explanation of the low temperature peaks was that polymer and monomer were capable of cocrystallization involving the side chains of the polymer and the alkyl group of the monomer. Such a phenomenon strongly indicated the true side chain crystallization in PDA. In such a situation the lower temperature sub-ambient peak represented the fusion of cocrystalline regions which were relatively rich in monomer whereas the higher temperature peak of the sub-ambient transition was thought to represent the fusion of essentially "free" monomer. The merging of the two transitions seemed reasonable at higher monomer concentration which resulted when the polymer was further degraded. The suppression of the higher temperature transitions when significant low temperature transitions were observed was thought to be a natural consequence of the fact that significant degradation had already occurred and that the liberated monomer dissolved and promoted the degradation of remaining polymer, as well as causing a broadening of the transitions of remaining polymer.

4. Extrusion of PDA and characterization of the extrudate. PDA

powder had the same general characteristics as PNA powder at room temperature. At temperatures at the upper range of the first transition region there was sufficient molecular mobility in PDA so that the polymer could be extruded to a coherent filament as was observed with other comb like polyaldehydes[77]. PDA was extruded at 53°C through capillaries having different aspect ratios. The original extrudates were reextruded at 60°C. X-ray investigations of the various extrudates indicated that, contrary to the case of PNA, significant, set orientation was not achieved in the extrusion process.

PDA powder was extruded at 53°C through two different capillaries having L/D values of 34 and 40 respectively. In each case an irregular trace of the force required to maintain constant crosshead speed was recorded. An indication of a yield stress was also observed, this was more evident when the capillary having a L/D of 40 was used. An average value of the apparent viscosity of 1.4×10^4 poise was calculated when the capillary having an aspect ratio 34 was used, when the capillary having aspect ratio 40 was used, an average value of 5.8×10^4 poise was calculated. These values were calculated by using the value of the force indicated by the best horizontal line which could be drawn through the irregular force traces. In the second extrusion performed at 53°C, using the capillary having aspect ratio 40, the force was observed to drop to a second approximately constant value toward the end of the extrusion.

Both extrudates obtained at 53°C were pelletized, combined, and reextruded at 60°C through a capillary having an aspect ratio of 34. In this case a very irregular force trace was recorded which varied by

as much as 10 kg.

In all extrusions the extrudate appeared soft and somewhat rubbery and could easily support its own weight at least 40cm. below the capillary exit. When PDA was reextruded at 60°C the extrudate appeared to have a thin liquid coating on its surface which was believed to be decanal and was easily removed with acetone washing. The filaments obtained from each extrusion were easily coiled while warm, some of the curvature introduced by the coiling became "set" when the extrudate cooled and became more brittle.

The ideal conditions of steady state capillary flow were not approached in the extrusion experiments. This situation was indicated by the fact that the force traces were very irregular and that an indication of yield stress behavior was observed. Thus, it was thought that the values calculated for the "melt" viscosity of PDA were of limited validity.

The various anomalies observed during the extrusion of PDA were thought to be due to the interplay of various factors relating to the crystallinity of the polymer and possibly extraneous factors as well. Melting and recrystallization of the side chains was believed to be more in balance during extrusion of PDA that in the case of PNA and the polymer mobility was more restricted which was reflected in the irregular force trace. In this case restriction of side chain mobility resulted in restriction of crystalline and noncrystalline main chain units. Reextrusion of the original extrudates (which showed different first transition behavior than the original powder) was even more complicated which suggested a relation between side chain melting (or

crystallization) and the anomalous extrusion behavior. The fact that the extrusion process influenced the first transition of PDA in an atypical way also suggested that the phenomena associated with the first transition were influencing the extrusion behavior of PDA under the conditions employed.

The thermal stability of PDA extruded at 53^{o}C was examined by TGA. The temperature of onset of weight loss and temperature of 5% wt. loss (100^{o}C and 115^{o}C respectively) for the acetone washed and dried extrudate were slightly higher than for the original powder. This situation was thought to be the result of removal of highly unstable fractions through thermal degradation of polymer during the extrusion. A break was observed in the TGA curves of the extrudates which was not observed in the TGA curve of the original powder. Two explanations for this break were considered. It was thought that the break in the TGA curve might have been due to the presence in the sample of fractions of different thermal stabilities which became more noticeable by TGA when very unstable polymer was removed by thermal degradation. It was also thought that the break in the TGA curve may have been the result of a change in degradation mechanism caused by impurities, particularly metallic impurities, introduced during the extrusion process. Changes in sample crystallinity and geometry may also have affected the shape of the TGA curve.

Degradation of PDA during DSC measurements on powder samples was strongly suspected. For this reason it was attempted to investigate the thermal stability of PDA extrudate under conditions simulating more severe, average conditions that samples were subjected to in DSC

experiments. Known weights of PDA, extruded at 53°C, were placed into tared DSC sample pans which were then sealed. The sample pans were then conductively heated under an atmosphere of N_2 in a beaker fixed in a water bath which was held at 72°C. Sample pans were removed at various time intervals, opened, and their contents extracted with acetone. After 10 min., 60% acetone insoluble material remained; after 25 min., only 20% acetone insoluble material remained. On the basis of these observations it was confirmed that significant polymer degradation probably occurred during DSC measurements on the extrudates as was thought.

The extrusion process affected the melting behavior of PDA in a peculiar and unique way in comparison to other long side chain polyaldehydes. This was particularly true in regards to the behavior of PDA in the first transition region. The peak temperatures of the extruded material were higher than those of the original powder and the higher temperature peak of the first transition was clearly dominant in the thermograms of the extruded sample. The enthalpy associated with the first transition was always greater for the extruded samples than for samples of the original powder. Furthermore, the enthalpy associated with the first transition of extruded PDA was always less when a sample of the extrudate was heated through the first transition, cooled, and then rescanned. Thus, the changes in the behavior of PDA in the first transition region which occurred when the polymer was extruded were different than the changes which were observed in the case of PNA. It was attempted to anneal samples of extruded PDA which had been once heated through the first transition in order to determine whether the

enthalpy associated with the first transition could again be increased to the higher value observed for the virgin extrudate. However, when samples of the extrudate were heated to 72°C, quenched to 53°C and annealed, the maximum first transition enthalpy attainable (10 min. annealing) was ca. half that of the original extrudate. At longer annealing times polymer degradation was significant and its effects dominated over all other effects.

The second transition of PDA was less readily observed in samples extruded at 53°C, particularly if the presence of even a small amount of monomer was suggested by the appearance of a relatively small low temperature transition. In fact, even the polymer degradation endotherm was sometimes conspicuously missing in thermograms of extruded PDA.

The second transition of extruded PDA was more easily observed by optical microscopy and occurred at lower temperatures and over a broader temperature range (15°C) than in the case of the original PDA powder. The influence of polymer degradation and polymer crystallization were thought to account for the suppression of higher temperature endotherms in the thermograms of PDA because of broadening and cancellation of signals.

Typical DSC scans recorded for PDA extruded at 53°C through a capillary having L/D=34 are reproduced in Figure 17 and are described in Table 14. The thermograms recorded for PDA extruded at 53°C through a capillary having L/D=40 were identical to those of the polymer extruded through the first capillary in regards to peak shapes and transition enthalpies while the peak temperatures were, on the average, 2°C higher. The apparent increase in peak temperatures for PDA extruded at

Figure 17: DSC of Extruded Polydecanal (PDA) ($20^{o}C$/min.)

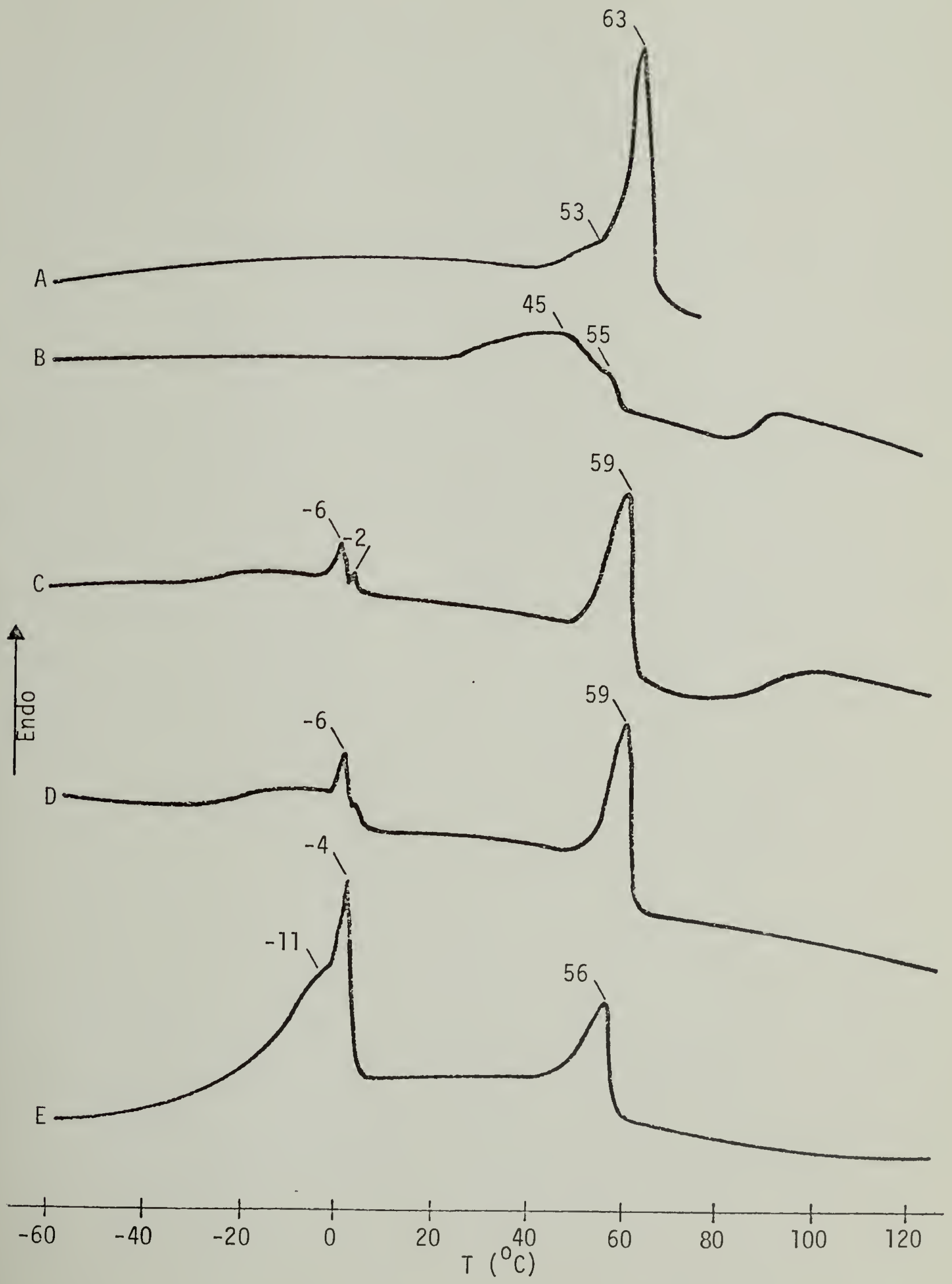


TABLE 14

DSC of PDA Extruded at 53°C[a]

Scan[b]	Sample Description	First Transition Peak Temperatures (in °C)	ΔH First Transition (in cal./g.)
A	First scan to 80°C	53[c]; 63	15.5
B	After first scan to 80°C (A) quench and rescan	45; 55[c]	12.0
C[d]	Heated to 80°C, quenched to 52°C and annealed 7 min., quenched	59	7.4
D[e]	Heated to 80°C, quenched to 52°C and annealed 12 min., quenched	59	7.4
E[f]	Heated to 85°C, quenched to 52°C and annealed 18 min., quenched	56	5.9

[a]Data of DSC scan of Fig. 17. Capillary L/D=34.

[b]Same as in Fig. 17

[c]Shoulder

[d]Low temperature transition recorded, peaks at -6° and -2°C

[e]Low temperature transition recorded, broad peak -6°C

[f]Low temperature transition recorded, peak at -4°C, shoulder at -11°C. Total area corresponded to 18.1cal./g. based on initial sample weight.

53°C through the L/D=40 capillary may have been fortuitous and merely due to changes in instrument calibration. The melting behavior of PDA extruded at 53°C was not found to be significantly dependent upon heating rate when heating rates equal to or greater than 20°C/min. were used. However, endothermic shifts in the region of the second transition of PDA were more obvious at higher heating rates. The enthalpy associated with the first transition endotherms always equalled the enthalpy associated with first transition exotherms when heating or cooling rates of 20°C/min. or 40°C/min. were used. Polymer degradation interfered at lower heating rates; precision was sacrificed at higher heating rates.

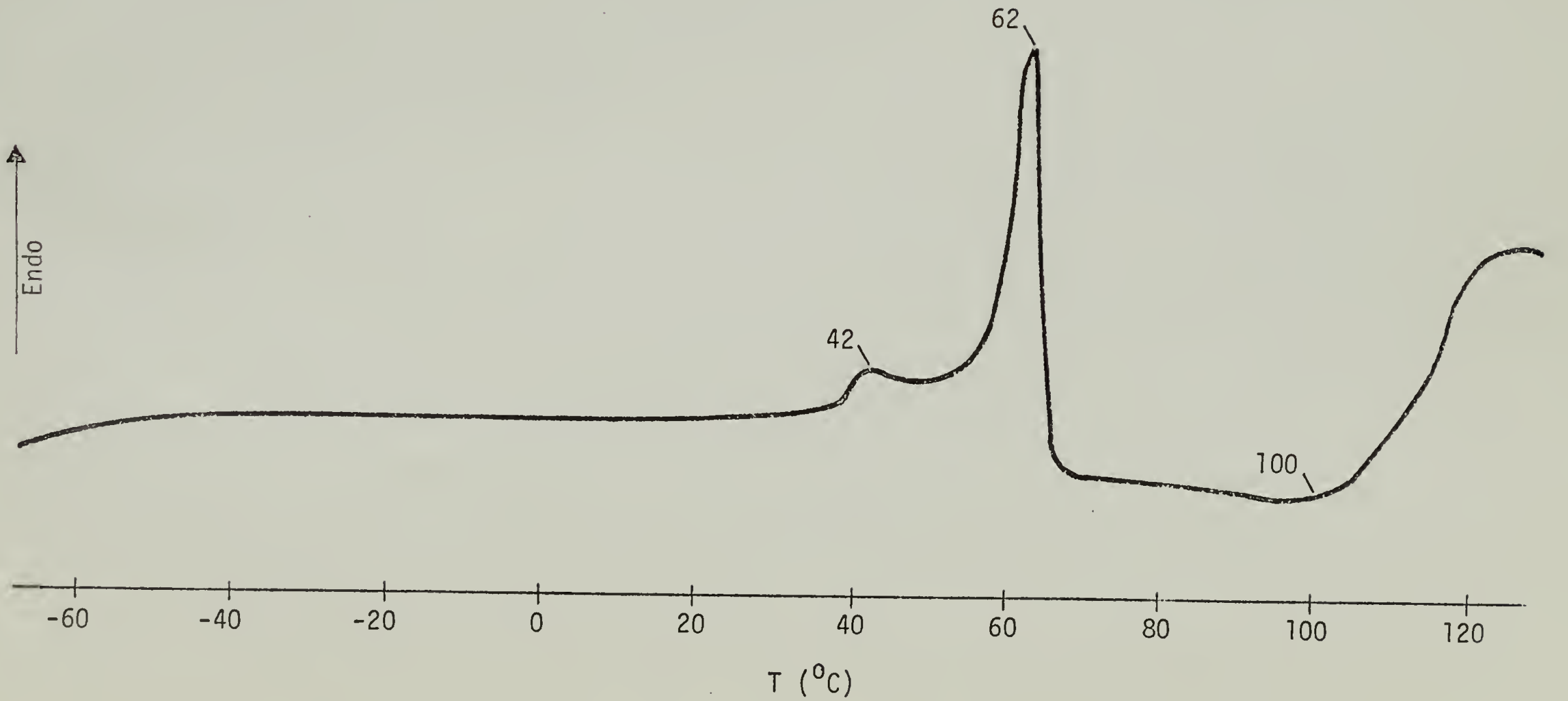
In the case of PDA the major effect of extrusion of PDA at temperatures within the first transition region appeared to be an annealing of the crystallinity responsible for the first transition. This was indicated by the fact that peak temperatures and transition enthalpies were invariably higher for extruded PDA as compared to the initial powder. X-ray investigations indicated however that orientation of PDA during the extrusion was not very significant. These observations were believed to be related to two factors; firstly, the increasing dominance of the side chain in controlling polyaldehyde crystallization and secondly, the temperature of extrusion was within the range of the first transition which is related to the crystallization of the aliphatic side chains.

The enhancement of the first transition of PDA induced by the extrusion process was even more evident in the thermograms of the extrudate obtained by reextrusion of the original extrudates at 60°C

through a capillary having L/D=34. The peak shapes of this extrudate were identical to those of the 53°C extrudate, however, peak temperatures were 5°-6°C higher and heats of fusion of 17-18cal./g. were observed. The DSC scan of a sample of the reextruded polymer is reproduced in Figure 18. Transitions at temperatures above the first transition were more clearly evident in thermograms of PDA extruded at 60°C, the exact reason for this is not known. It was speculated that higher temperature transitions were more evident for two reasons. Firstly, since the polymer had been treated at different conditions a change in polymer crystallinity was thought possible. Secondly, polymer degradation during DSC could have been less significant in the reextruded PDA than in the case of the original extrudate because of still further removal of polymer of lowest thermal stability during the second extrusion.

X-ray diffraction diagrams of PDA extruded at 53°C and 60°C indicated that the orientation of polymer introduced by extrusion was much less significant than had been observed in the case of PNA. This situation severely limited the progress which could be made toward elucidating the crystal structure of PDA. However, the number of observed reflections and their intensity in the diffraction diagrams of extruded PDA strongly suggested that PDA was capable of crystallizing in manner by which both main chains and side chains participate in the unit cell. In the case of other comb like polymers where polymer crystallinity arises solely from the packing of the side chains only a few reflections are generally observed at larger angles, the strongest of which corresponds to a spacing near 4.2Å. In such polymers two

Figure 18: DSC of Polydecanal (PDA) Reextruded at 60°C (20°C/min.)



reflections are generally observed at smaller angles which correspond to the type of layer packing of the side chains[114].

Numerous attempts were made to prepare oriented samples of PDA by mechanical treatment of PDA extrudate; both cold rolling and cold drawing were attempted. PDA extrudate was quite brittle and the sample failed during the mechanical treatment. X-ray and DSC investigations indicated that no change in the orientation of the sample or in the melting behavior of PDA-E was achieved by additional mechanical treatments.

5. Melting behavior and crystal structure of PDA. Two transition regions were identified for PDA. In analogy to other long side chain polyaldehydes it was believed that the first transition of PDA (40^{o} to 75^{o}C) represented a change in the packing or crystallization of the aliphatic side chains whereas the second transition region (110^{o} to 130^{o}C) reflected the true melting of the polymer involving the collapse of a crystal lattice in which the main chains participated. X-ray investigations indicated that PDA was capable of existing in a crystalline form in which both main chains and side chains participate in the unit cell. As mentioned before, the number and intensity of wide angle reflections were too significant to assume that crystallization of PDA involved only the alkyl side chains. The pattern of the x-ray diffraction of PDA, particularly for the extruded samples, suggested that the unit cell which incorporated both main and side chains was perhaps tetragonal, as in the case of PNA and PHA, or possibly a slight modification of this (e.g. orthorhombic[129]). If true side chain crystallization was responsible for the first transition of PNA, then the

occurrence of this phenomenon was even more likely in the case of PDA which has a still longer side chain. The assumption that true independent side chain crystallization was responsible for the first transition of PDA was consistent with experimental observations. Some of the reflections observed in the x-ray diffraction diagrams of PDA, particularly the reflection which corresponded to a spacing of 4.2$\mathring{A}$, were undoubtably due to the crystallization of the side chains.

The infrared spectrum of PDA cast as a film from $CHCl_3$ suggested that the side chains of PDA were hexagonally packed, at least under this condition of sample treatment. It was thought that the infrared spectrum of the polymer in the region of 720cm.$^{-1}$ did not truly discriminate between the packing of the side chains in regions of independent side chain crystallization vs. packing of the side chains within a unit cell in which main chain units also participated. Comparison of the available data suggested that in regions of side chain crystallization the side chains are hexagonal packed. An attempt was made to measure the infrared spectrum of extruded PDA directly so that this might be compared with the spectrum of solvent cast films of PDA in order to compare the packing of side chains in the two samples. However, absorption of energy by the extrudate was such that the sample softened while in the beam.

In some respects PDA was unique in comparison to other comb like polyaldehydes, this was particularly true in regards to the effect of extrusion on the behavior of the polymer in the first transition region. The changes in behavior for PDA were due to the greater influence of the aliphatic side chains. A significant change in polymer

properties over a narrow range of side chain lengths had been observed in the case of comb like poly(α-olefins). Thus, the fact that PDA behaved in a peculiar manner in comparison to PHA was not alarming, particularly since a trend to increasing influence of the side chain on polymer properties was observed in the case of PNA.

Extrusion of PDA appeared to have an annealing effect on the side chain crystallization. Thus, to first approximation, the thermal effects of the annealing process appeared to be more significant than the mechanical effects in the case of PDA. It was thought possible that, at the temperatures used for extrusion, the orientation induced by the mechanical effects may have induced a "zippering" of the side chains before significant orientation of main chains (or crystallites involving them) was induced. If such was the case, then it could be said that independent crystallization of the side chains impeded the crystallization of the main chains, a situation opposite to that thought to be the case in comb like polyaldehydes with shorter side chains.

It is possible that if higher temperatures were used during extrusion then a more favorable relative rate of main chain crystallization might have resulted and a more oriented sample of PDA, with more typical behavior, would have been obtained. However, even when PDA was extruded at 60^{o}C, a temperature several degrees above the highest peak temperature observed for powdered PDA, the annealing effect of the extrusion process was still clearly evident.

F. Polyundecanal (PUA)

1. Introduction. Polyundecanal (PUA) could be prepared by anionic polymerization only from carefully purified monomer using a procedure in which monomer, solvent, and initiator were mixed near -20°C followed by controlled cooling of the reaction mixture. Typical aldehyde polymerization procedures (e.g. addition of monomer to well cooled solvent / initiator mixture) were unsuccessful for the anionic polymerization of undecanal to crystalline polymer.

The novel procedure was used in two successful preparations of PUA at two different initial monomer concentrations with two different monomer / initiator ratios. The temperature histories of the two reactions, including the endcapping steps, were only slightly different. The chemical structure of the product was the same in both cases. It was found that, just as in the case of PDA, if the endcapping reaction was conducted under relatively mild conditions, PUA was sufficiently stable to be isolated, handled, and stored for several days at room temperature.

Two transition regions were identified for PUA. However, the crystallization and melting behavior of PUA was somewhat different than for other polyaldehydes. X-ray diffraction diagrams suggested that, overall, the crystallization of PUA was different than for PNA or PHA.

PUA could be extruded and gave coherent filaments. X-ray diffraction measurements showed that orientation during extrusion was even less in the case of PUA than was observed in the case of PDA.

2. Synthesis and characterization of PUA.

a. Synthesis and chemical characterization. Undecanal is even less soluble in those solvents typically used in the anionic polymerization of aliphatic aldehydes than either nonanal or decanal. If undecanal was added to a cold ($T<-50^{o}C$) mixture of solvent and initiator, the crystallization of monomer from its solution effectively competed with polymerization. The polymerization of undecanal to crystalline polymer was only achieved if monomer, solvent (MCH), and initiator (LTB) were mixed at a relatively higher temperature (ca. $-20^{o}C$) then carefully cooled (cryotachensic polymerization).

This procedure was successfully used for two preparations of PUA. In the first case, the relative amount of monomer was 18% to solvent (ca. 0.8M in monomer) and 3 mole% initiator was used. PUA having an inherent viscosity of 1.3dl./g. was obtained in 15% yield (PUA-I). In the second case the relative amount of monomer was 9% to solvent (ca. 0.4M in monomer) and 6 mole% initiator was used. PUA having an inherent viscosity of 0.82dl./g. was obtained in 46% yield (PUA-II). In both preparations the endcapping reaction was conducted only at room temperature or below for up to 3 hrs.. The overall temperature histories of the two preparations were only slightly different. When the lower monomer concentration was used with higher mole% initiator then a higher polymer yield was realized. However, as expected, the molecular weight of the polymer was lower as suggested by the lower inherent viscosity.

The chemical properties and structure of PUA-I and PUA-II were the same. The infrared spectra of both samples of PUA (pg. 259) were very similar to each other and to the spectra of other aliphatic polyalde-

hydes and indicated the polyacetal structure of the polymer. The infrared spectrum of a $CHCl_3$ solution of PUA is compared with that of PNA in Figure 9.

The 90 MHz PMR spectrum of PUA-II is shown in Figure 10 and further indicated the polyacetal structure of the polymer. As discussed before, reproducible integration of the PMR spectra of the higher polyaldehydes was difficult to achieve. However, inspection of the spectra revealed that, as expected, the relative area of the acetalic main chain protons and side chain methyl groups decreased as the length of the side chain increased.

When either PUA-I or PUA-II was subjected to acidolytic degradation in the presence of 2,4-dinitrophenylhydrazine the same aldehyde 2,4-dinitrophenylhydrazone was obtained which melted at 104°C.

b. Thermal stability of the polymer. The thermal stability of PUA was investigated by TGA. Both samples of the polymer had identical TGA curves. As in the case of PNA and PDA the temperature of onset of weight loss (degradation) and the temperature of 5% weight loss were the most convenient indicators of polymer thermal stability as measured by programmed TGA and this data was the most consistent with other observations regarding polymer thermal stability.

PUA, as obtained from either preparation, had a temperature of onset of weight loss of 104°C and a temperature of 5% wt. loss of 125°C. The spread between these two values (20°C) was larger than that observed in the case of other higher aliphatic aldehyde polymers. Since the polymer synthesis, stabilization, and purification procedure, as well as sample geometry, in the case of PUA was very similar to the case of

PNA and PDA, the larger spread was thought to be artifact relating to volatility of degradation products and not due to a significant change in polymer degradation mechanism, etc.. However, the crystallinity of PUA may have been different than in the case of PNA or PDA and hence such factors as O_2 adsorption and permiation, which may affect TGA results, might have been partly responsible for the slightly different TGA observations in the case of PUA.

When stored for 2 weeks in loosely closed vessels at room temperature in the dark PUA-I and PUA-II transformed into yellowish oils consisting largely of monomer which was identified as its 2,4-dinitrophenylhydrazone.

c. X-ray diffraction by PUA powder. The X-ray powder diagram (pg. 276) of acetone washed PUA-I (which was identical to that of PUA-II) was noticeably different from that of PNA or PDA. This suggested that, under similar conditions, PUA crystallized differently than PNA or PDA. However, the x-ray powder diagrams of PUA were similar to those of several other comb like polyaldehydes in that two closely spaced, slightly diffuse reflections were recorded in the region which corresponded to 4.2Å to 4.7Å.

The spacings and relative intensities corresponding to the reflections recorded in the x-ray diffraction diagram of PUA are recorded in Table 15. The fact that the x-ray diffraction diagram of PUA was quite different from that of other comb like polyaldehydes was thought to be due to the influence of the side chains on polyaldehyde crystallization; which was even more significant in the case of PUA.

3. Investigation of the melting behavior of PUA by DSC. The

TABLE 15

X-ray Diffraction by PUA[a]

Reflection #	Relative Intensity	d (in Å)	Comments
1	s	14.84	
2	m	8.42	
3	w	7.28	
4	m	4.63	diffuse, may be two closely spaced reflections
5	m	4.22	diffuse

[a]Acetone treated polymer. Exposure time, 8 hrs.; sample-to-film distance, 108mm.

melting behavior of PUA was investigated by DSC. The instrumental parameters typically used were the same as in the case of other higher aliphatic aldehyde polymers and again thermal treatment of the samples was performed in the calorimeter. Peak positions gave the most reproducible and consistent representation of the melting behavior. Optical microscopic observation of samples as a function of temperature were also useful in relation to the DSC studies.

The DSC scans of PUA were influenced by the sample geometry. This was particularly true in relation to peak shapes and apparent baseline departure temperatures. The measured transition enthalpies of samples of PUA also showed some dependence on sample geometry. The sample geometry also seemed to influence baseline shapes and slopes moreso than in the case of PDA or PNA, and hence there was more ambiguity in baseline interpolation. Thus, even through the precision of peak area measurements (with a given interpolated baseline) were the same as in the case of PNA or PDA, less confidence could be placed in the transition enthalpy measurements. The level of precision of the transition enthalpy measurements in the case of PUA was assumed to be half that in the case of PDA or PNA, e.g. 6%; the accuracy of the temperature measurements was the same.

Two transition regions were identified for PUA. The second transition was less significant in the case of PUA than in the case of polyaldehydes with shorter side chains. Thermograms of PUA-I and PUA-II were very similar to each other, particularly in regards to transition regions and peak shapes.

The first transition of PUA was in the region of 30^{o} to 65^{o}C and

had an associated heat of 14-18cal./g.. The first transition was normally recorded as two overlapping endothermic peaks. However, the transition was sometimes recorded as a single, broad peak with or without shoulders. The appearance of the DSC scans in the first transition region depended, to some extent, on sample geometry. If the first transition was recorded as only a single peak, which was more frequently the case with very coarse powder or clumped samples, then the transition enthalpy seemed to be greater by as much as 20% in comparison to the transition enthalpy when the transition was recorded as multiple endotherms.

The details of the first transition endotherms of PUA did not exhibit a noticeable dependence on heating rate when heating rates of 10°C/min. to 80°C/min. were used. If a sample of PUA was heated at 20°C/min. through the first transition, cooled, then rescanned (both at 20°C/min.), the enthalpies associated with both endotherms and the exotherm were all equal within experimental error. In such cases the exotherm was a single, nearly symmetrical peak whereas the first transition endotherms consisted of multiple peaks.

The second transition of PUA occurred at a temperature where polymer degradation was significant. Normally, the second transition of powder samples of PUA was recorded as a shoulder on the broad decomposition exotherm. In rare cases, if small (ca. 1mg.) samples of fine PUA powder were scanned, the second transition was more clearly resolved and a definite peak was recorded on the shoulder of the decomposition exotherm.

When samples of PUA (I or II) were observed between crossed polars

at a programmed heating rate these behaved very similar to similarly treated samples of PDA or PNA, at least up through the first transition. At temperatures between 45° and 60°C samples of PUA appeared to soften and changes in the transmission of polarized light through the sample were observed. At 65°C a greater extinction was observed than at corresponding temperatures for similarly treated PNA or PDA. Between 75° and 85°C transmission increased in samples of PUA. The second transition of PUA was observed at 100° to 105°C by optical microscopy. At these temperatures the sample became optically isotropic and rapid polymer degradation occurred.

Typical DSC thermograms recorded for PUA-I are shown in Figure 19 (corresponding data in Table 16); those for PUA-II are shown in Figure 20 (corresponding data in Table 17). As previously mentioned and suggested in the figures, the first transition of PUA was normally recorded as two overlapping peaks. The peak positions depended on the origin of the sample and its thermal history. Since peak shapes depended on both sample history and sample geometry, it was not always possible to separate the two effects.

The details of the melting behavior, particularly in the first transition region, were slightly different between PUA-I and PUA-II. However, similar trends were observed in both cases. Thus, if either sample of PUA was heated through the first transition, quenched, then rescanned, the peak temperatures were observed to be lower but the transition enthalpies were only slightly decreased. If samples of PUA were annealed from below, then the temperatures of the lower temperature peak of the first transition was increased and the apparent

Figure 19: DSC of Polyundecanal (PUA-I)
(20°C/min.)

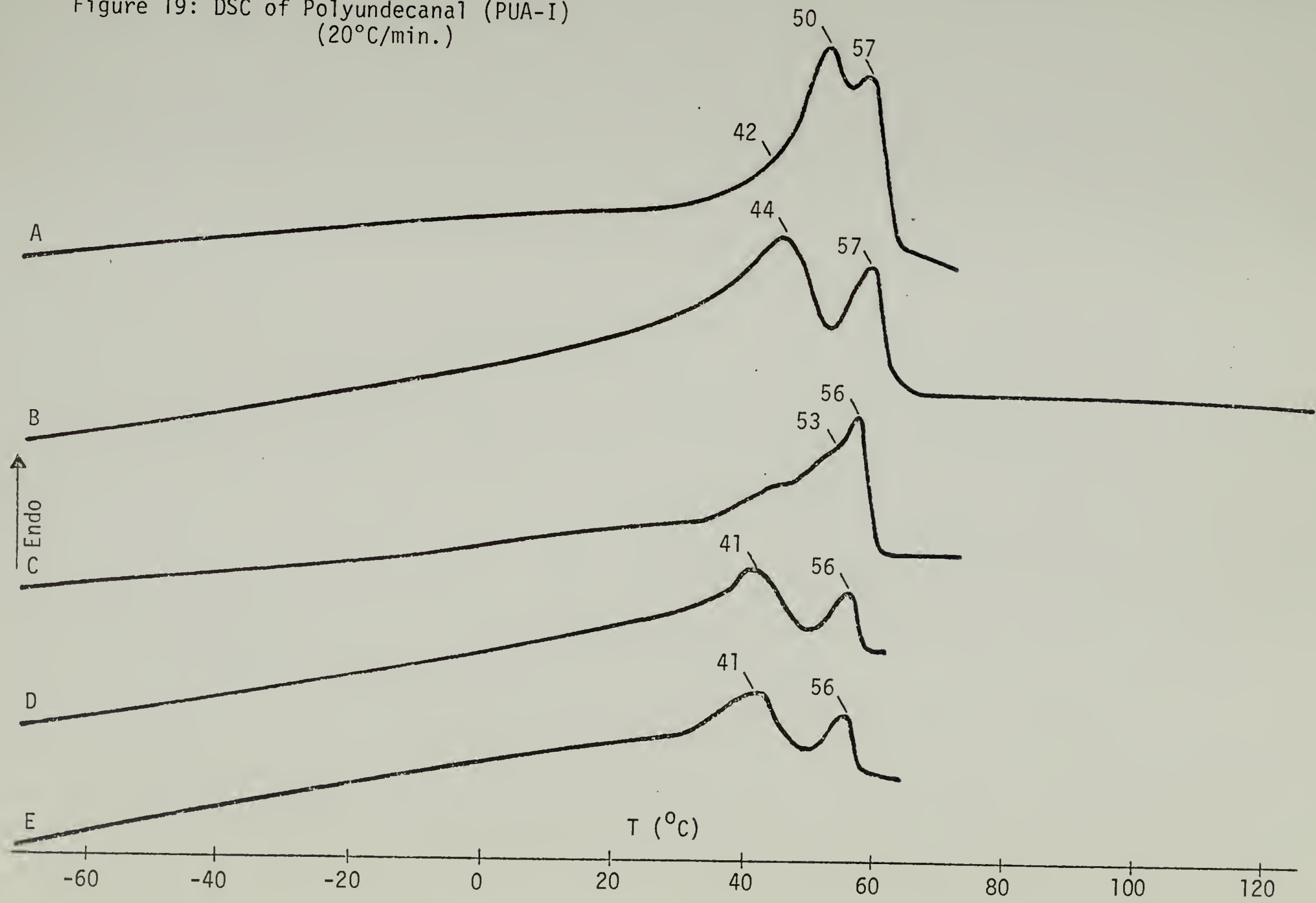


TABLE 16

DSC of PUA-I[a]

Scan[b]	Sample Description	First Transition Peak Temperatures (in °C)	ΔH First Transition (in cal./g.)
A	First scan to 70°C	50; 57	14.7
B	After first scan (A) quench to 52°C, anneal 5 min., quench	44; 57	14.4
C	First scan to 75°C	53[c]; 56	16.4
D	After first scan (C) quench to 54°C, anneal 10 min., quench	41; 56	12.8
E	After second scan (D) quench to 44°C, anneal 10 min., quench	41; 56	12.9

[a]Data of DSC scans in Fig. 19.

[b]Same as in Fig. 19.

[c]Shoulder.

Figure 20: DSC of Polyundecanal (PUA-II) ($20^{o}C$/min.)

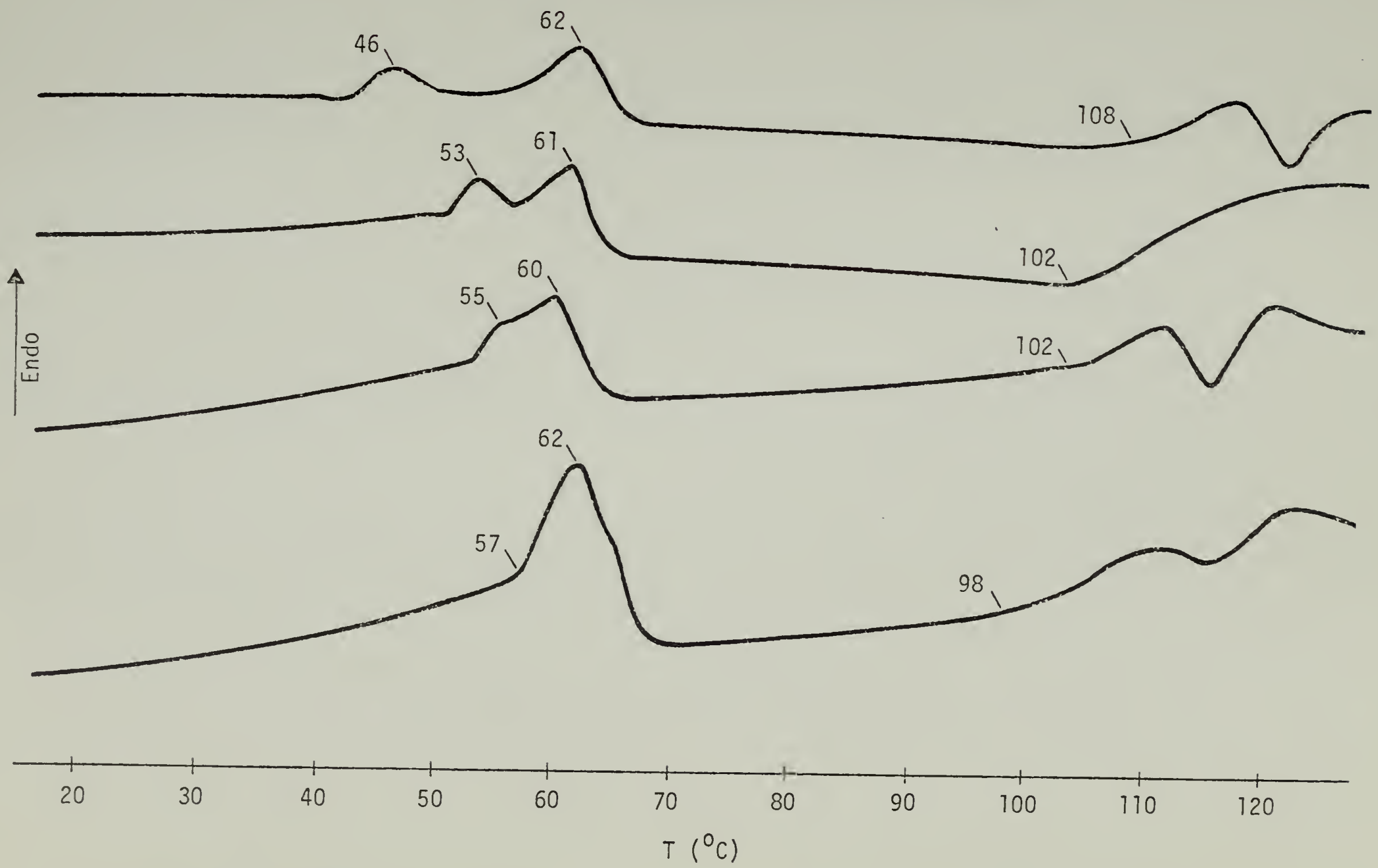


TABLE 17

DSC of PUA-II[a]

Scan[b]	Sample Description	First Transition Peak Temperatures (in °C)	ΔH First Transition (in cal./g.)
A	Virgin	46; 62	14.8
B	Heated to 45°C, annealed 5 min., quenched	53; 61	14.9
C	Heated to 48°C, annealed 5 min., quenched	55[c]; 61	14.5
D	Heated to 52°C, annealed 6 min., quenched	57[c]; 62	17.7

[a]Data of thermograms of Fig. 20.

[b]Same as Fig. 20.

[c]Shoulder.

relative area of the higher temperature peak was increased. If samples of PUA were heated to a temperature above the first transition region then quenched to the desired annealing temperature the effects of annealing did not follow such a simple pattern.

Transitions occurring below room temperature were recorded in thermograms of PNA and PDA when the presence of monomer in the samples could be expected. In the case of PUA low temperature transitions were much less frequently observed and were recorded, typically as a single peak, only in the thermograms of samples which had been subjected to conditions which promoted extensive degradation. Since the thermal stability of PUA was similar to that of the other polyaldehydes investigated it was assumed that, under similar conditions of thermal treatment, comparable degradation to monomer should have been produced in PUA. It was thought that the presence of low to moderate levels of undecanal in PUA was at first indicated by a decrease in the apparent point of baseline departure at the first transition. The presence of monomer in samples of higher aliphatic polyaldehydes always resulted in a lowering of the apparent point of baseline departure. However, the magnitude of the apparent depression was greatest in the case of PUA and the assignment of baseline departure point at the first transition was the most difficult for this polymer. The apparent point of baseline departure at the first transition of PUA was decreased by as much as 15^{o} to 20^{o}C when PUA was treated under conditions which had resulted in the appearance of low temperature peaks in thermograms of PDA or PNA. The magnitude of this discrepancy was larger than that which was normally observed on the basis of sample geometry alone.

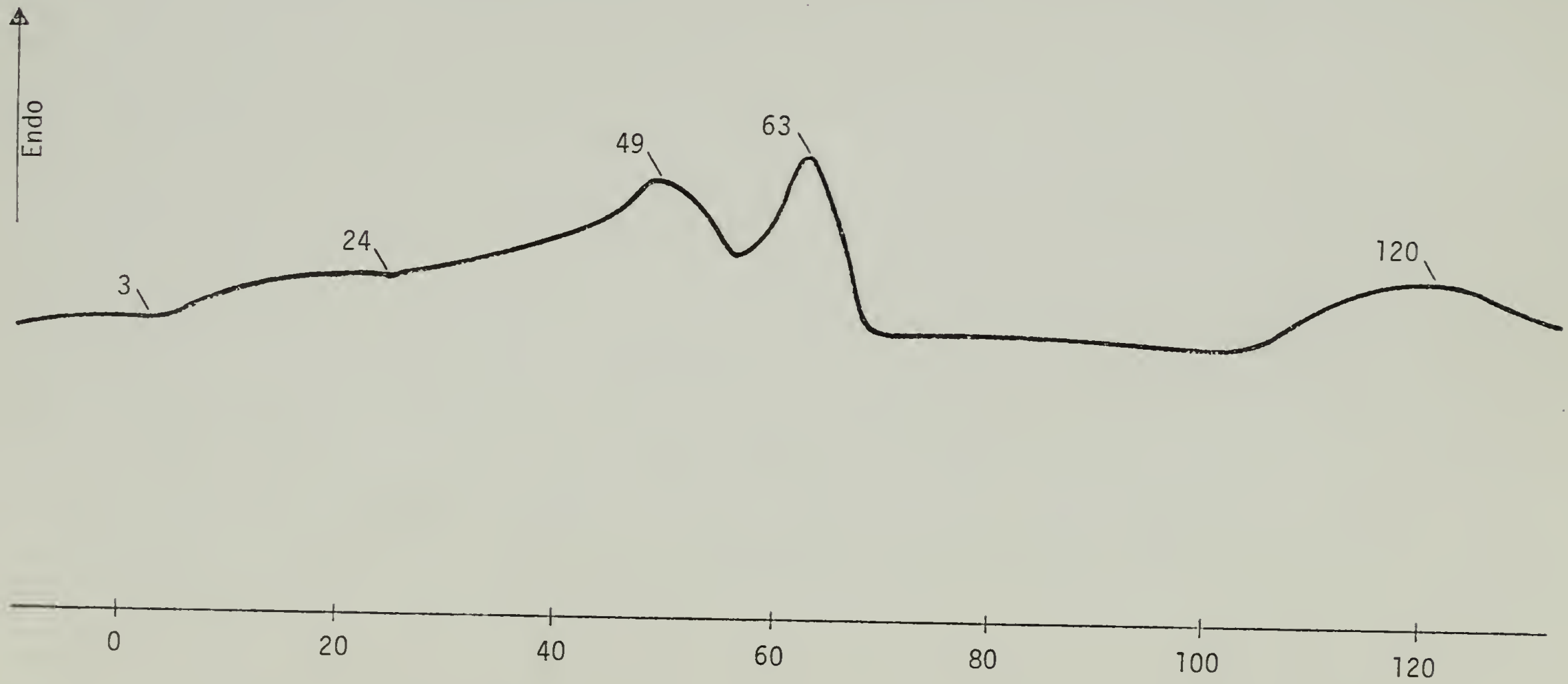
Figure 21 shows the DSC scan of a sample of PUA which had been heated from room temperature to 61°C, held at 61°C for 12 min., then rapidly cooled and rescanned. According to experience gained in the case of PNA and PDA this thermal treatment should have been sufficient to produce at least a modest level of monomer in the polymer. No low temperature transitions were recorded.

The significant decrease in the lower limit of the first transition region of PUA and the corresponding increased difficulty in determining the point of baseline departure at the first transition region as discussed were thought to possibly be related to a very broad transition which was a result of the presence of monomer in the sample. Because the side chains of undecanal and PUA are relatively longer and because the melting point of monomer and the first transition of polymer were more similar in the case of PUA it was thought that physical interaction of monomer and polymer could extend over a broader range of temperatures and compositions which gave rise to the broad transition. The fact that PUA may crystallize in a slightly different way than PNA, may also have promoted greater physical interaction of monomer and polymer.

4. Extrusion of PUA and characterization of the extrudate. PUA could be extruded if heated to the first transition. However, x-ray diffraction experiments indicated that very little, if any, orientation of PUA was introduced by the extrusion process.

PUA-II was extruded at 60°C through a capillary having a L/D value of 34. The trace of the force required to maintain a constant crosshead speed was regular and smooth, the apparent viscosity was

Figure 21: DSC of Thermally Treated Polyundecanal (PUA-II) ($20^{o}C$/min.)



4920 poise. The filament extrudate was barely able to support its own weight to a length of 40cm. below the capillary exit and failed at that length. If still warm the filament was soft and flexible enough to be easily bent back on itself in a short radius; curvature created by such bending became set when the extrudate cooled. At room temperature PUA extrudate (PUA-E) became stiff and could be broken with a minimum of splintering. The greater flexibility of PUA "melt" and the fact that PUA-E qualitatively behaved in a more plastic, brittle manner was thought to be due to a difference in the crystallization of PUA in comparison to PNA or PDA.

The thermal stability of PUA-E was investigated by TGA. An increase in the stability of PNA and PDA was indicated when these were extruded; this phenomenon was also observed in the case of PUA. The thermal degradation of PUA-E was checked under several conditions to determine whether thermal treatment, such as that which might be imparted during DSC measurements, would affect the polymer degradation in a way measurable by TGA. If PUA-E was thermally treated in the TGA apparatus, the temperature of onset of weight loss and temperature of 5% wt. loss were decreased and changes in the shape of the TGA curves were observed. The TGA experiments indicated that degradation of PUA and contamination of the polymer with monomer under conditions of the DSC experiments was likely. The measurements also suggested that PUA powder also became contaminated with monomer during DSC measurements even though distinct low temperature peaks were not recorded.

The x-ray diffraction diagram (pg. 276) of PUA-E indicated that a minimal orientation was induced during the extrusion process. The

x-ray diffraction diagram of PUA-E was very similar to that of PUA powder and quite unlike those of extruded PNA or PDA, particularly in view of the relatively small number of reflections that were recorded.

The melting behavior of PUA-E was investigated by DSC. Most measurements were made using the DSC-2 calorimeter and were checked against results obtained with the DSC-1B calorimeter. The extrusion process, under the conditions employed, had a less noticeable effect on the melting behavior of PUA.

Two transition regions were recorded for PUA which was extruded at 60°C. The temperature regions of the transitions and the peak shapes of the endotherms in the first transition of PUA-E were very similar to those of the original PUA powder. Again, the endotherm of the first transition appeared as two peaks. The peak temperatures were slightly higher and the lower temperature peak of the first transition was more predominant in the case of PUA-E as compared to the original powder. The enthalpy of the first transition of PUA was hardly affected by the extrusion process; values of 15-18cal./g. were observed for the first transition of PUA-E.

Uncharacteristic baseline shapes, which were observed when fresh samples of PUA-E were scanned for the first time in the DSC-2 (Fig. 22, curve A), made baseline interpolation difficult and impeded accurate measurement of the first transition enthalpies. Values of the first transition enthalpy of PUA-E obtained from DSC-1B measurements agreed with those from DSC-2 measurements. Data from several thermograms of PUA-E are collected in Table 18.

Various thermal treatments affected the first transition of PUA-E

Figure 22: DSC of Polyundecanal Extruded at 60°C (PUA-E) (20°C/min.)

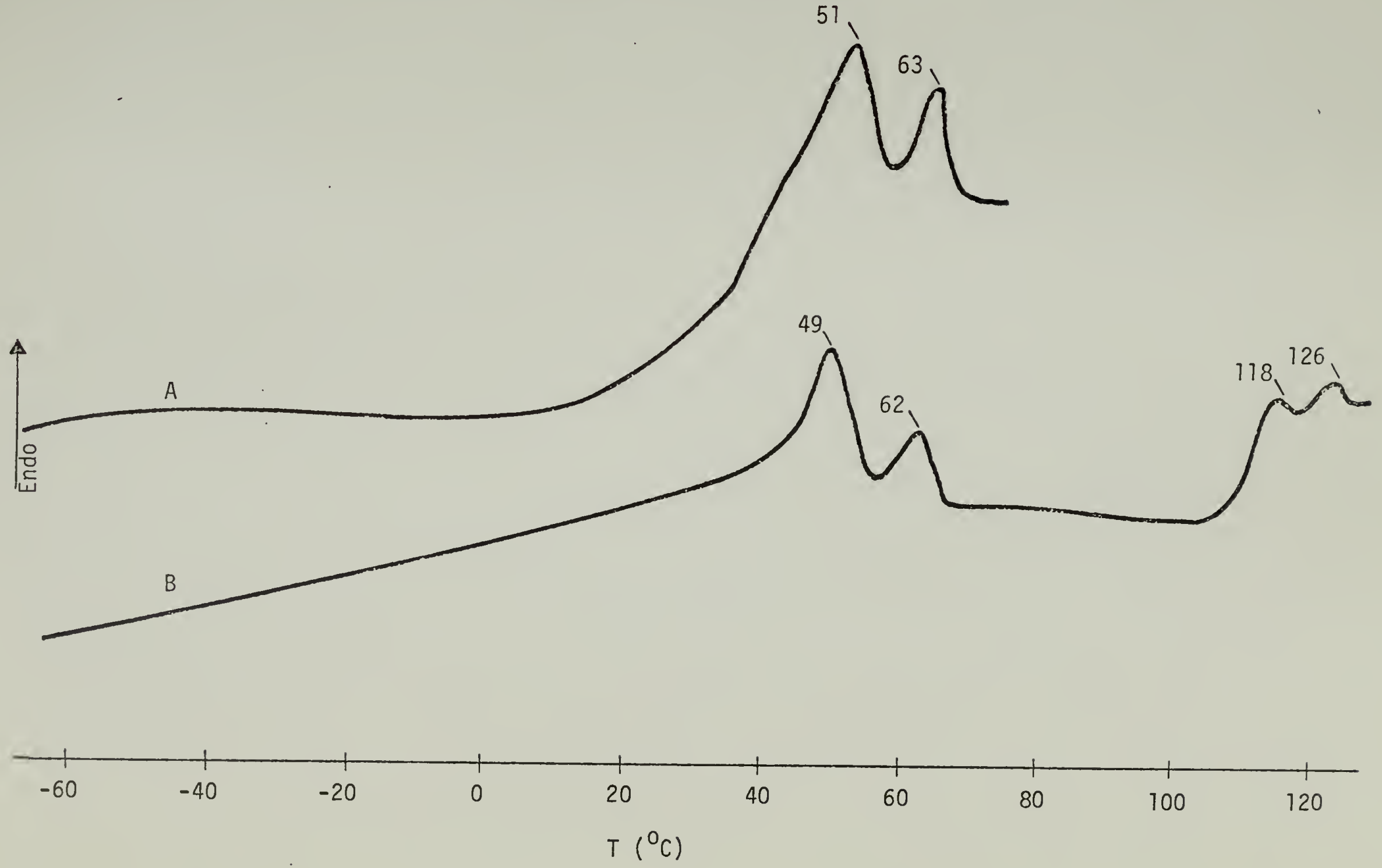


Figure 22 (cont'd):

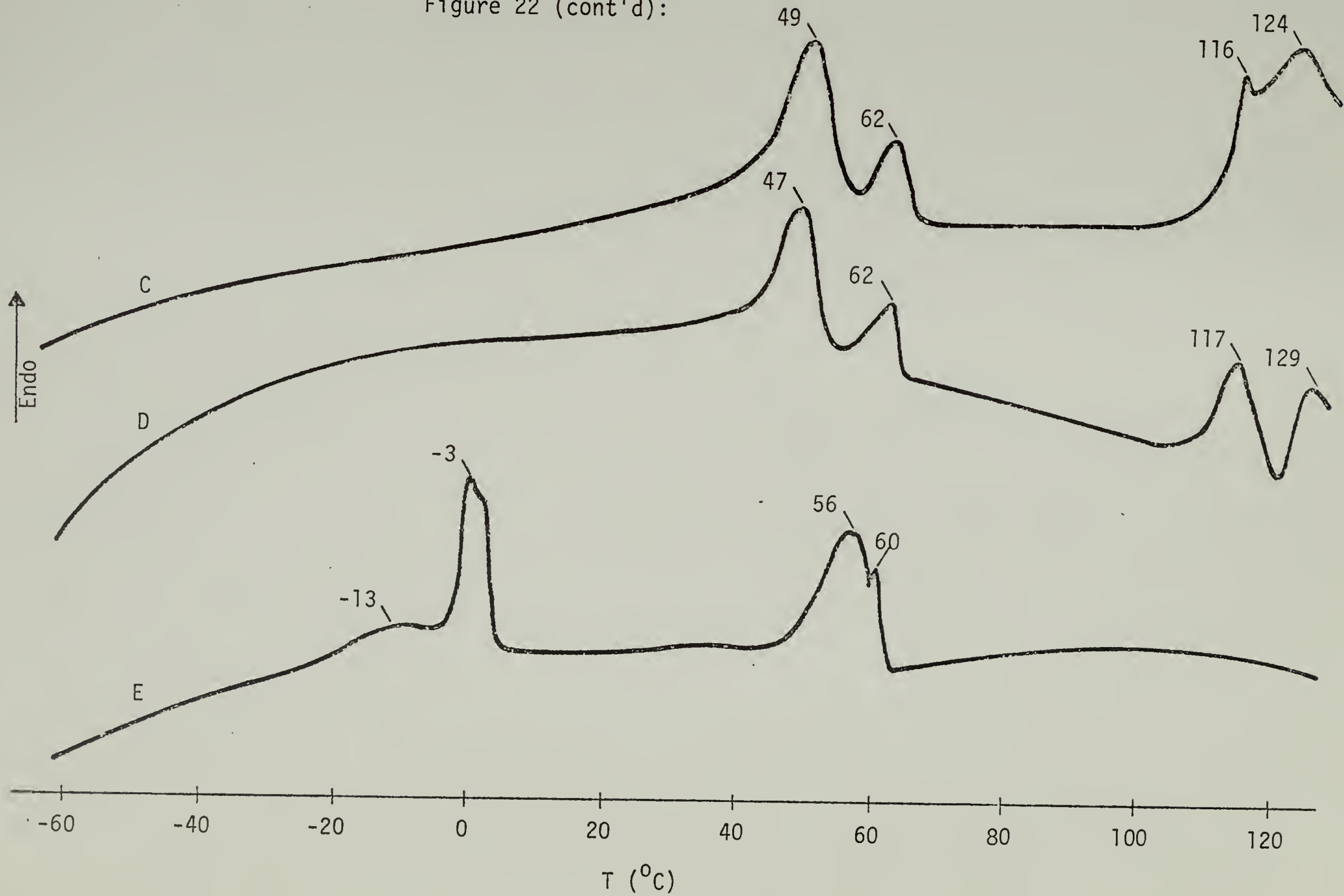


TABLE 18

DSC of PUA-E[a]

Scan[b]	Sample Description	First Transition Peak Temperatures (in °C)	ΔH First Transition (in cal./g.)	Second Transition (in °C)
A	First scan to 72°C	51; 63	15.3	-
B	After first scan to 72°C (A), quench and rescan	49; 62	15.4	115
C	Heated to 72°C, quenched to 58°C and annealed 7 min., quenched	49; 62	16.0	115
D	Heated to 75°C, quenched to 65°C and annealed 7 min., quenched	47; 61	15.3	115
E[c]	Heated to 72°C, quenched to 55°C and cycled between 55° and 58°C at 1.25°C/min. for 20 min., quenched	56; 60	10.7	-

[a]Data of thermograms of Figure 22.

[b]Same as Figure 22.

[c]Double peaked sub-ambient transition recorded; peaks at -31°C (broad) and -3°C

in a very similar manner as in the case of the original powder. In a number of instances the first transition enthalpy of PUA powder was lower than that of PUA-E when both had been given similar thermal treatment, although peak temperatures and shapes had been affected in a similar way. This was thought to be due to formation of a relatively higher amount of monomer under given conditions in the case of PUA powder which was less thermally stable. The second transition of PUA was more clearly evident in samples of PUA-E; the exothermic break at the second transition was sharper and shoulders were more noticeable.

In isolated cases a low temperature transition, which closely resembled that observed in the case of PNA and PDA, was recorded in DSC thermograms of thermally treated PUA-E (Fig. 22, curve E). The explanation of these low temperature transitions was the same as in the case of PNA and PDA. It was thought that monomer possibly interacted more efficiently with polymer side chains in the case of PUA. When monomer was present in PUA this seemed to result in the occurrence of a broad, difficultly distinguished transition which complicated the identification of baseline departure points. Such a transition is suggested in Figure 22, curve E, in the region of 23^{o} to 40^{o}C. The fact that low temperature transitions of the type encountered in the case of PNA and PDA were, rarely, recorded for PUA was most conveniently explained on the assumption that a specific thermal treatment (such as more prolonged annealing) caused formation of increased amounts of monomer and caused interaction of monomer with polymer side chain to become constrained to more narrow ranges of temperature and composition.

5. Melting behavior and crystal structure of PUA. Two transitions

were observed for PUA. The first transition of PUA (35^{o}-65^{o}C), which usually exhibited an associated enthalpy near 15cal./g., was due to melting of crystals which involved only the side chains whereas the second transition was due to collapse of a crystal lattice in which the backbone chains participated. The second transition of PUA was less significant than that of PNA or PDA. The polymer was softer and appeared to be more nearly optically isotropic at temperatures between the first and second transition than did the other polyaldehydes investigated.

The effect of monomer (from polymer degradation) on the DSC scans of PUA, particularly in the first transition region, could be best explained on the basis of specific interaction of monomer and polymer such as cocrystallization or related effects. The occurrence of this type of interaction was taken as a manifestation of the ability of higher aliphatic polyaldehydes to form crystalline regions without incorporation of main chain units. The influence of other structural parameters being held equal, this type of monomer polymer interaction was expected to become more favorable as the length of the side chain was increased. When monomer - polymer interaction resulted in cocrystallization phenomena in the case of PNA and PDA this was seen as an endothermic transition which occurred below room temperature in DSC scans of these polymers. Such a transition was rarely observed in the case of PUA. Instead, because of effects related to increased side chain length, monomer - polymer interaction was shifted to higher temperatures and different compositional ranges. Also, changes in the kind and relative decrease in amount of main chain crystallization, as

a result of increased side chain length, may have caused the polymer to be more permeable to monomer and caused more polymer side chains to be in an environment conducive to interaction with monomer alkyl groups. This monomer polymer interaction gave rise to a transition, which was broader and occurred at relatively higher temperatures, and which partly overlapped with the normal first transition of PUA.

When PUA was extruded at 60^{o}C the extrudate was initially softer than that of the other higher aliphatic polyaldehydes investigated. However, at room temperature the extrudate behaved in a more brittle plastic manner and fractured with a cleaner break than extruded PNA or PDA. In this respect PUA behaved in a manner more similar to other known classes of comb like polymers[114]. X-ray diffraction and DSC measurements indicated that extrusion of PUA caused negligible orientation and had very little effect on the polymer melting behavior in the first transition region.

At first inspection the results and conclusions regarding extrusion of PUA and the effect of extrusion on polymer melting behavior seemed to be in conflict with those for PDA where an increase in ΔH and peak temperatures in the first transition of PDA-E were attributed to effects of increased side chain length. This apparent conflict was believed to be due to the fact that the conditions during the respective extrusions were not, relatively speaking, comparable and that main chain crystallization in PUA was less significant. PUA seemed to have very little, if any, main chain crystallization of the type present in PDA and the side chains of the polymer were less constrained when heated to melting in the rheometer. In this case shear forces during extrusion

disrupted molecular alignment and polymer crystallization controlled by the side chains occurred as PUA cooled to room temperature after being extruded. Under the conditions of extrusion the side chains of PDA were probably not well molten and recrystallized during extrusion. However, an effect of increasing influence of the side chains was seen in that orientation and crystallization of main chains of PDA were diminished because of crystallization of the side chains. The presence of main chain crystallization in PDA may have enhanced side chain crystallization under the specific conditions by maintaining the side chains in relative positions conducive to their crystallization.

The x-ray diffraction diagrams of powder and extruded PUA were very similar to each other and noticeably different from those of either PNA or PDA. The most striking difference was the relatively small number of reflections observed in the case of PUA, particularly at values of 2θ less that about 12^{o}. In this region only 3 reflections were observed for PUA whereas 6 or more reflections were observed for both PNA and PDA. The difference in x-ray diffraction between PUA and either PNA or PDA suggested that the crystallinity of PUA was different than that of PNA or PDA. The number and distribution of diffraction rings suggested that crystallization of PUA was more dominated by packing requirements of the side chains and involved less contributions, if any, from the backbone. According to the x-ray experiments the main chain crystallization in samples of PUA was either so slight as to be difficultly detectable or produced a crystal structure quite different from that in the case of PNA.

6. Comparison of PUA to PNA and PDA and side chain crystallization of the polymers. The behavior and properties of PUA were generally consistent with those of PNA and PDA. However, the first transition of PUA assumed a more dominating role and main chain crystallization was less prevalent in this polymer. The results of characterization experiments on PNA, PDA, and PUA, as well as the effect of monomer on the polymers' melting behavior, were most conveniently reconciled if it was assumed that two distinct types of crystallinity were possible for these polymers. It seemed quite reasonable that packing of the paraffinic side chains should more and more dominate the crystallization of polyaldehydes as the length of the side chain was increased.

Increasing influence of the side chain on polymer melting behavior with increased side chain length had been observed in the case of poly(α-olefins) which are structurally similar to the polyaldehydes in many respects. The fact that the side chains of polyaldehydes influence the melting behavior of the polymer at relatively shorter side chain lengths in comparison to the olefin polymers was thought to be related to the difference in polarity of the main and side chains in the case of the polyaldehydes. This difference in polarity favored segregation of the side chains and hence promoted their independent crystallization.

When comb like polyolefins (having more than 12 side chain carbon atoms) were heated to a temperature above the side chain melting transition the polymers recrystallized to accommodate both main chains and side chains in the same crystal lattice. This recrystallization was clearly evident in DTA scans of the polymers[115]. Such pronounced recrystallization effects were not clearly observed in DSC scans of

polyaldehydes, however, some recrystallization of PUA between the first and second transition was indicated by optical microscopic investigation. It should be noted that x-ray diffraction by PUA in the region of $2\theta=20^{o}$ was very similar to that of the polyolefin having 20 side chain atoms. Where polyaldehyde recrystallization was possible during calorimetric analysis (to accommodate main and side chains in the same crystal lattice) this was probably impeded by the polarity difference between main and side chains. Polymer degradation occurred to a significant extent when thermal treatment of polyaldehydes was attempted at temperatures between the first and second transitions.

In the case of comb like acrylate, vinyl ester, and related polymers the crystallinity of the polymers had been found to be exclusively due to crystallization of the side chains which pack in a hexagonal lattice[114]. The x-ray diffraction diagrams of these polymers was characterized by a moderate to strong reflection corresponding to a spacing near 4.2Å. A similar reflection was observed in the case of PUA, PDA, and PNA and suggested that the side chains of the polymer were also hexagonally packed. The infrared spectrum of PUA was similar to that of PDA and PNA and the appearance of a singlet (with shoulder) in the region of 720cm.$^{-1}$ also suggested that (under the conditions of sample preparation) hexagonal packing of the side chains prevailed. However, infrared spectroscopy did not discriminate between side chains packed in regions of true side chain crystallization vs. regions of simultaneous main chain - side chain crystallization.

Jordan[78] has treated the data from calorimetric measurements on comb like acrylate, vinyl ester, and related polymers based on a model

for crystallization of the side chains employing literature data for the α_H - 1 transition of paraffins. It was found that the crystallinity of these polymers could be adequately expressed by the following equation:

$$X_{cs} = F \times \frac{\Delta H(n) \times (14.026)}{C + k(n)}$$

Where X_{cs} is the fraction of crystalline side chains; F is the inverse of the weight fraction of the polymer consisting of side chains; ΔH is the heat of fusion (in cal./g. sample) experimentally determined; n is the number of methylene groups (counting the terminal methyl group) in the side chain; 14.026 is the molecular weight of a methylene group. The denominator represents the equation of the line which fit the enthalpy data of the α_H - 1 transition of n-paraffins over a range of chain lengths similar to that of the polymers. The first term (C) was taken to be zero since only the changes in enthalpy over a short range of chain lengths were of interest; k is the value of the enthalpy per mole CH_2 and n is the number of carbon atoms in the hydrocarbon. This treatment has been extended to the first transition of polyaldehydes[68]. Treatment of the first transition data of polyaldehydes by this method is somewhat arbitrary since crystallinity in polyaldehydes has a contribution from the main chains and polyaldehydes exhibit multiple rather than single peaks in the first transition region. However, the quantity X_{cs} is a useful "index" for comparison of the side chain crystallization in various samples of polyaldehydes. Typical ranges for this parameter for PNA, PDA, and PUA are listed in Table 19. These calculations, performed assuming hexagonal packing, indicate the expected increased influence of the polymer side chains

TABLE 19

Side Chain Crystallinities of Aliphatic Polyaldehydes[a]

Polyaldehyde	Typical Range of ΔH, First Transition (in cal./g.)	Range of χ_{cs}
Polynonanal	5 - 8	0.12 - 0.19
Polydecanal	9 - 11	0.21 - 0.25
Polyundecanal	14 - 18	0.31 - 0.40

[a]Calculated according to Jordan[78] assuming k = 745

on crystallization behavior.

The dual transition behavior of polyaldehydes, which was first observed more than 15 years ago for polyaldehydes having a side chain length as short as 4 carbon atoms[15], had been confirmed and investigated in greater detail for the case of PHA which showed considerable crystallization of its main chain[16]. When PUA was prepared and its melting behavior investigated, two transitions were also recorded for this polymer. These two transitions could be related to the occurrence of two types of crystallization in the polymer. Packing of the side chains, which was responsible for the first transition of PUA, exerted a dominating but probably not exclusive role in the crystallization of this polymer. The side chains of polyaldehydes influence the melting behavior and crystallization of the highly-crystalline polymers to a greater extent at a relatively shorter side chain lengths than in the case of poly(α-olefins) which, amongst the known classes of comb like polymers, are the closest structural analogous of the polyaldehydes. The ability of the side chains of PUA to strongly influence the crystallization of the polymer, at a side chain length of 10 carbon atoms, suggested that PUA was very close to a point where the crystallization of polyaldehydes could be expected to be exclusively controlled by packing of the side chains.

G. Polydodecanal

1. Introduction. Numerous attempts were made to prepare polydodecanal (PDDA) by anionic polymerization of dodecanal with LTB initiator; both exploratory and preparative scale polymerizations were

conducted. PDDA having adequate stability was never obtained in sufficient yield for thermal characterization experiments. In exploratory scale experiments the order of reagent charging was found to have little influence on the results of the experiments; which was thought to be partly due to monomer solubility. The inherently low solubility of dodecanal under a variety of polymerization conditions was a serious complication which was not easily circumvented even by more careful control of the temperature history of the polymerization reaction.

Although no polymer was isolated from preparative scale polymerizations, certain observations made during the course of the reactions suggested that a polymer of dodecanal had been obtained. The reasons for the failure of dodecanal to yield adequately stable, isolatable polymers when subjected to conditions very similar to those which were known to afford polymers of aliphatic aldehydes having shorter side chains is not well understood.

2. Attempted synthesis of PDDA. Several exploratory scale investigations of the LTB initiated anionic polymerization of dodecanal in hydrocarbon solvents were conducted. The details of one such investigation which gave encouraging observations and results are described in chapter II. In this investigation dodecanal which had been pretreated and distilled once was used; the mole percent initiator (ca. 2%) was the same in each run. Charging of monomer into prechilled initiator solution and the reverse charging (initiator into chilled monomer solution) were both used. Several endcapping reagents were also explored. In the series of experiments in question the polymerization reaction was subjected to several cooling-warming cycles in an attempt to obtain

a favorable monomer-polymer equilibrium. Formation of opalescent gel (not observed when solutions of monomer or initiator were cooled) indicated that polymerization had occurred.

A white solid was obtained in some of the runs by pouring the reaction mixture into a chilled mixture of DMF and methanol. The white solids obtained when acetic anhydride was the endcapping reagent were quite similar and PMR spectroscopy indicated that both had the same polyacetal structure. The low viscosity of $CHCl_3$ solutions, the more sluggish reaction with 2,4-dinitrophenylhydrazine, and the fact that degradation of the products at room temperature uncharacteristically levelled off with time suggested that the product was not a pure polyaldehyde. However, the film forming characteristics observed during preparation of samples for infrared measurements and the fact that degradation occurred when the products were allowed to stand at room temperature indicated that polymer was obtained. The DSC scans of the white products were very similar to those of dodecanal cyclic trimer excepting that transition regions were broader and transition enthalpies lower.

Preparative scale polymerization of dodecanal was attempted in both MCH and toluene solvents at different initial monomer concentrations employing close control of the reaction temperature history. Only freshly purified or prepared reagents or solvents were used. Significant precipitation or crystallization of monomer occurred in all cases. However, as in the case of undecanal polymerization, monomer was compatible with the reaction mixture to a lower temperature if toluene was the solvent instead of MCH. The increase in viscosity of

the reaction mixture and the formation of discrete gel particles (particularly if MCH was the solvent) indicated that polymerization had occurred and that PDDA probably existed in solution or in a highly swollen state at temperatures near or below -40°C.

In all cases stabilization of polymer was attempted by addition of acetic anhydride and pyridine to the polymerization mixture in order to endcap the polymer; conditions similar to those of other higher aliphatic aldehyde polymerizations were used. After a time the reaction mixture was poured into cold acetone; a difficultly filtered, turbid solution was obtained which yielded a small amount of highly swollen material. Washing of the isolated material resulted in a trace yield of off-white solid; insoluble in toluene, cyclohexane, $CHCl_3$ and H_2CCl_2. Usually, a near quantitative recovery of monomeric dodecanal (as its bisulfite addition compound) could be obtained from the filtrate.

Several factors were thought to account for the failure to isolate PDDA with sufficient purity and stability and in sufficient yield for preliminary characterization experiments; each of which was in one way or another related to the length of the alkyl group. Dodecanal has the highest melting point and the lowest solubility in typical aldehyde polymerization solvents of all aliphatic aldehydes whose polymerization was investigated and crystallization of monomer from its solution was in competition with polymerization. Such phenomena affected the rate of polymerization and the position of monomer-polymer equilibrium. It was also thought that the physical properties of the polymer itself influenced the polymerization and impeded isolation of the polymer.

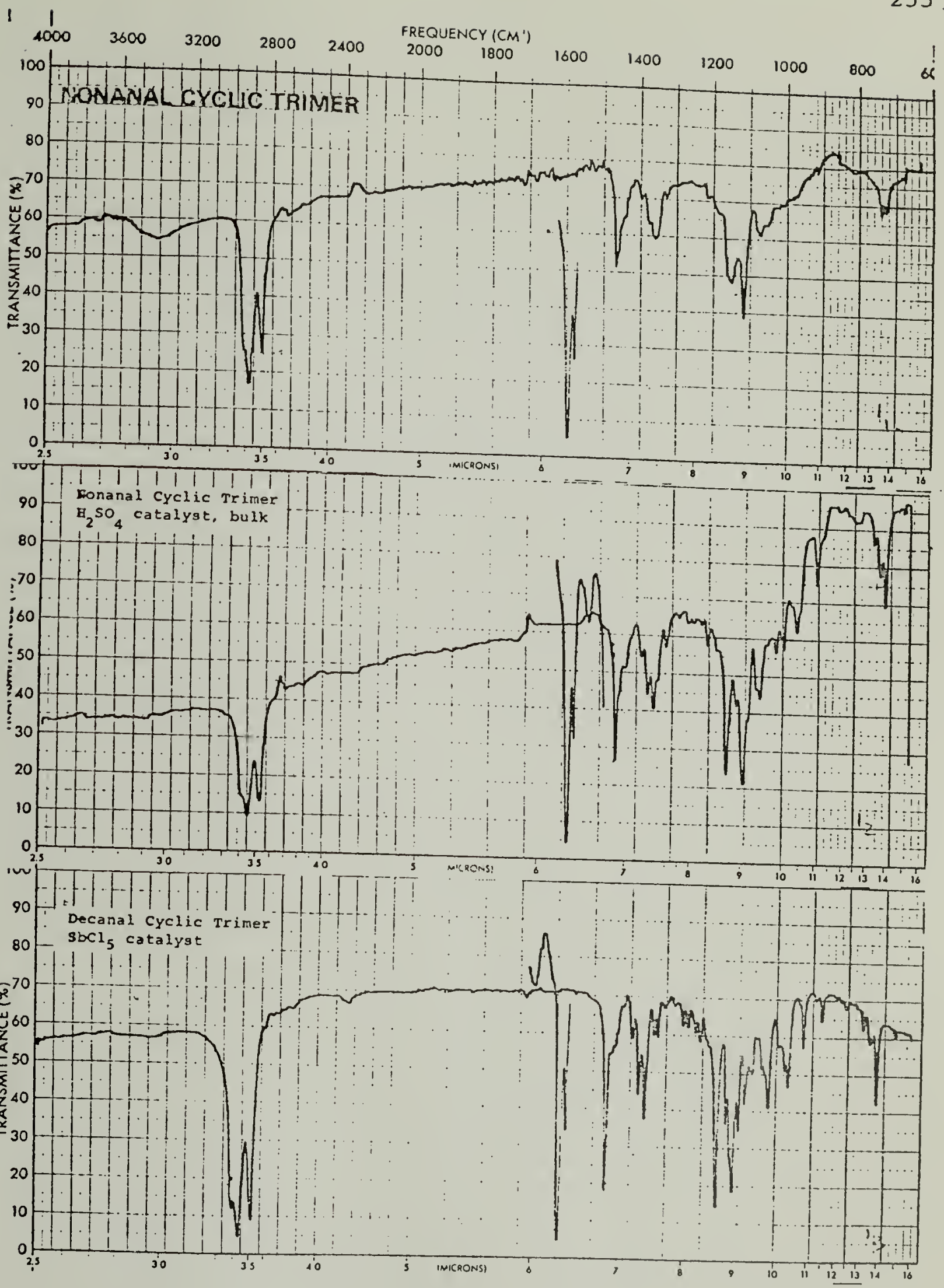
Any rigorous treatment of the thermodynamics of aldehyde

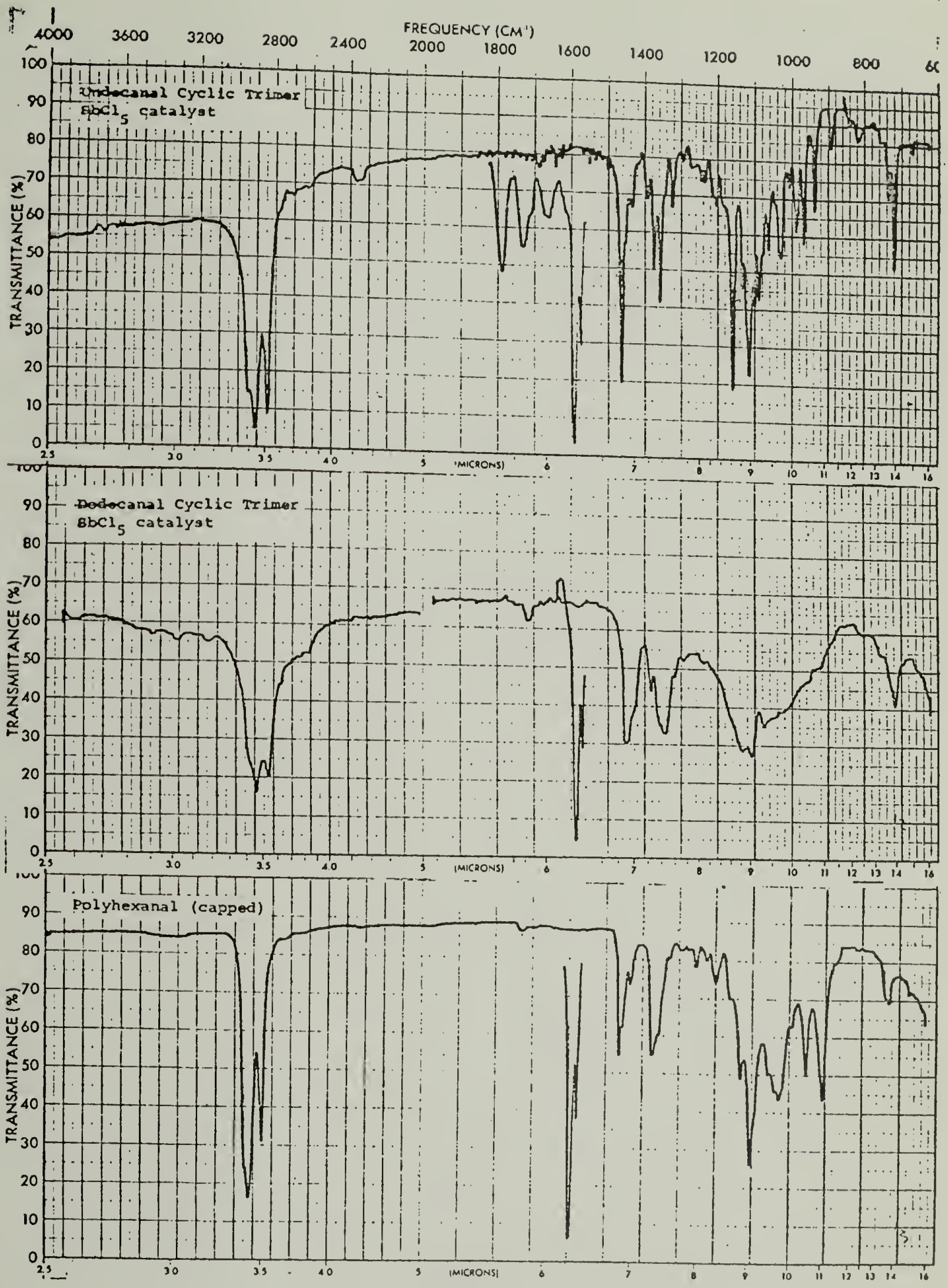
polymerization must take into account the crystallization of polymer which occurs during the polymerization. It is possible that crystallization of PDDA occurred to a different extent or in a different way than in the case of other polyaldehydes and the monomer-polymer equilibrium was affected in an unfavorable way. This could have resulted from intrinsically different crystallization of PDDA which may have been swollen or dissolved during polymerization to a different extent than in the case of polyaldehydes with shorter side chains. Crystallization of the polymer during polymerization, which is an additional and important driving force for the preparation of higher isotactic polyaldehydes, is also influenced by the swelling of polymer by monomer and solvent. If the physical properties of PDDA were indeed such that the polymer was more readily swollen then this would have impared precipitation of the polymer and facilitated more extensive degradation of the polymer during stabilization and isolation at room temperature.

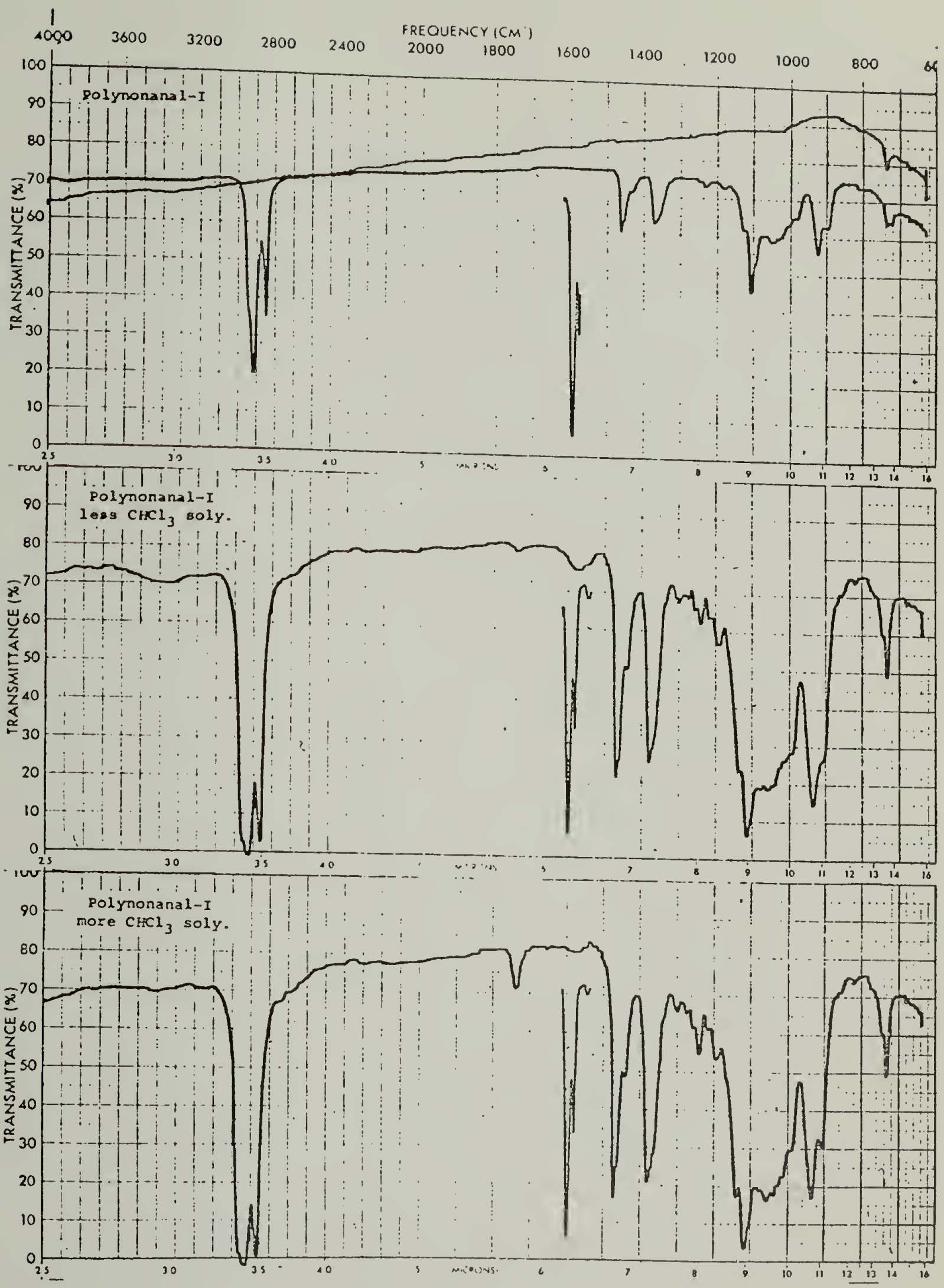
In at least one experiment it was attempted to isolate polymer by quenching the polymerization and precipitating the polymer directly by addition of chilled acetone to the cold polymerization mixture. However, although gel-like particles were evident when the mixture was warmed to ca. $-30^{o}C$, no polymer was isolated.

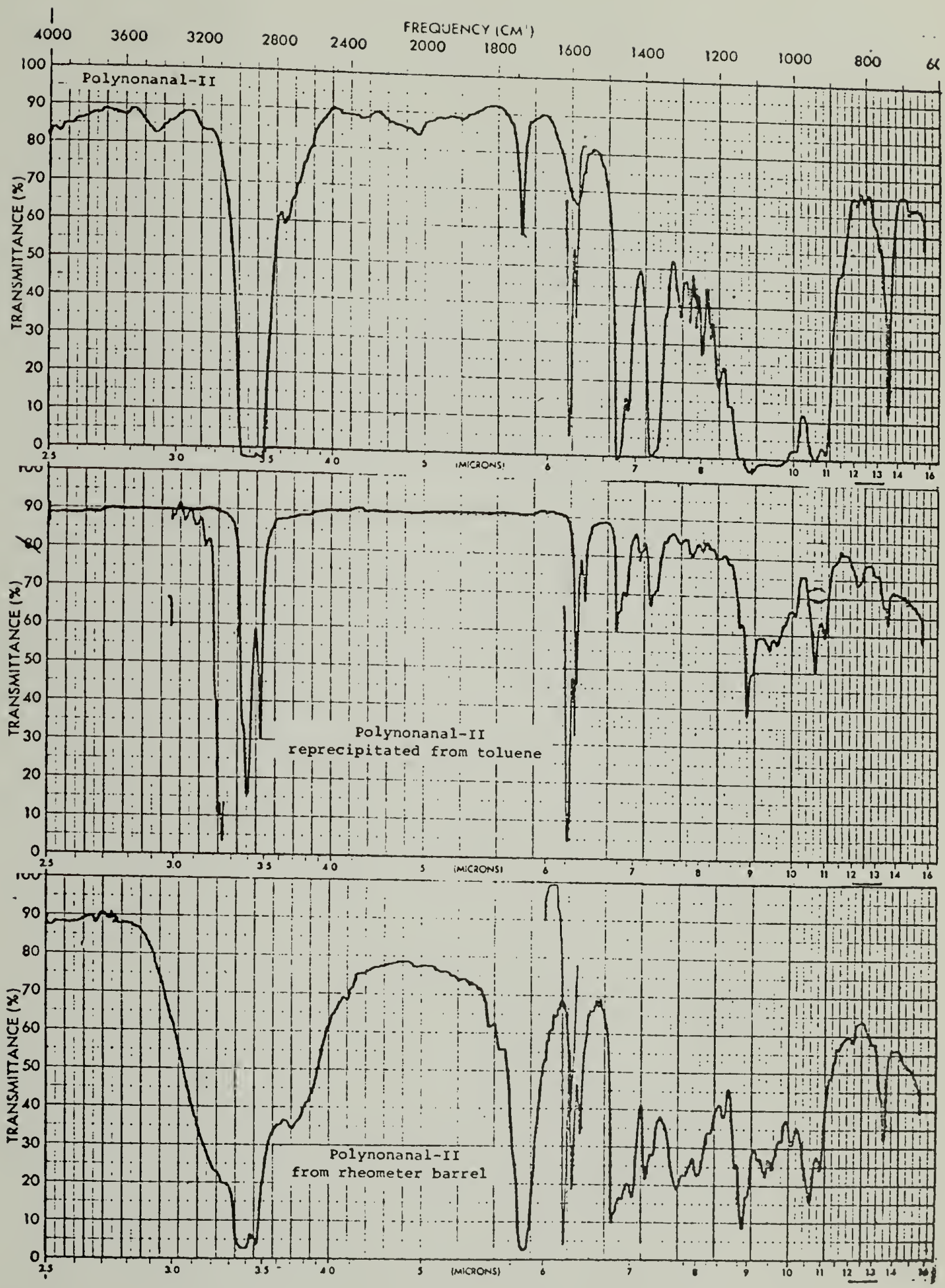
APPENDIX I

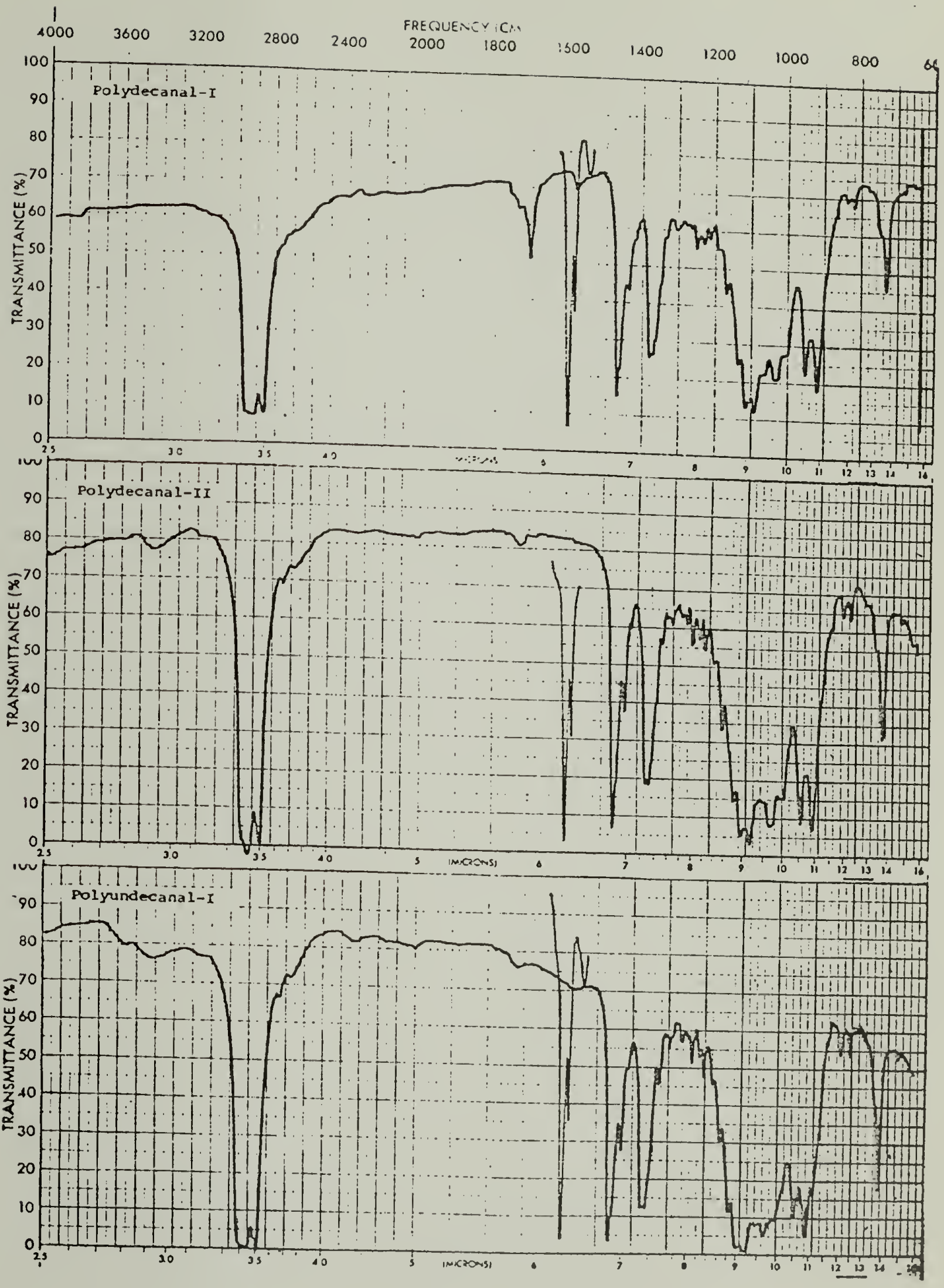
INFRARED SPECTRA

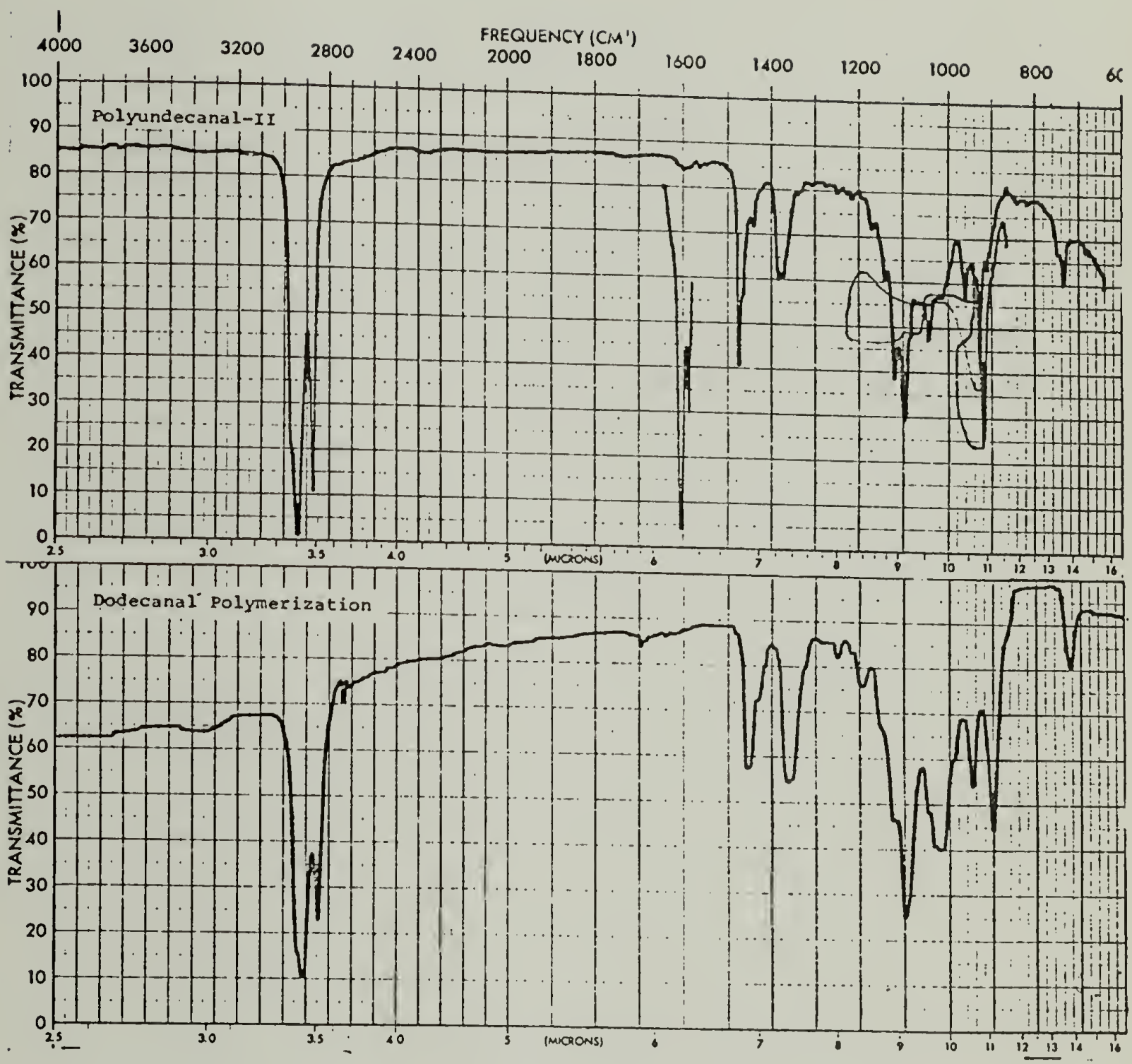

NONANAL CYCLIC TRIMER
FREQUENCY (CM⁻¹)
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
TRANSMITTANCE (%)
MICRONS)
Nonanal Cyclic Trimer
H_2SO_4 catalyst, bulk
Decanal Cyclic Trimer
$SbCl_5$ catalyst


FREQUENCY (CM⁻¹)
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
TRANSMITTANCE (%)
Dodecanal Cyclic Trimer
SbCl5 catalyst
(MICRONS)
Dodecanal Cyclic Trimer
SbCl5 catalyst
Polyhexanal (capped)


FREQUENCY (CM⁻¹)
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800
Polynonanal-I
TRANSMITTANCE (%)
Polynonanal-I
less CHCl3 soly.
Polynonanal-I
more CHCl3 soly.
MICRONS

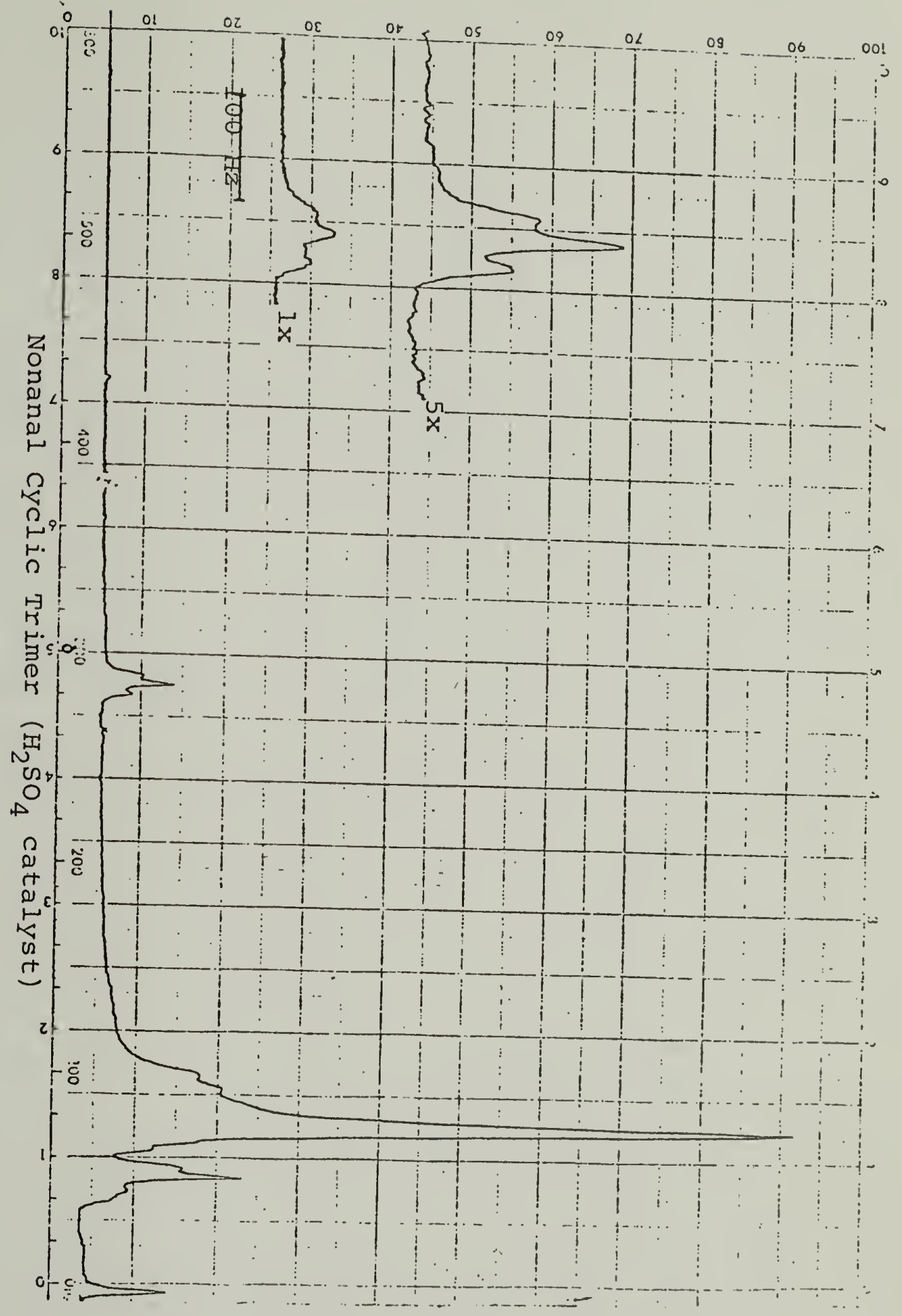

FREQUENCY (CM⁻¹)
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800
Polynonanal-II
TRANSMITTANCE (%)
(MICRONS)
Polynonanal-II
reprecipitated from toluene
Polynonanal-II
from rheometer barrel


FREQUENCY (CM)
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
Polydecanal-I
TRANSMITTANCE (%)
Polydecanal-II
Polyundecanal-I
IMICRONS)

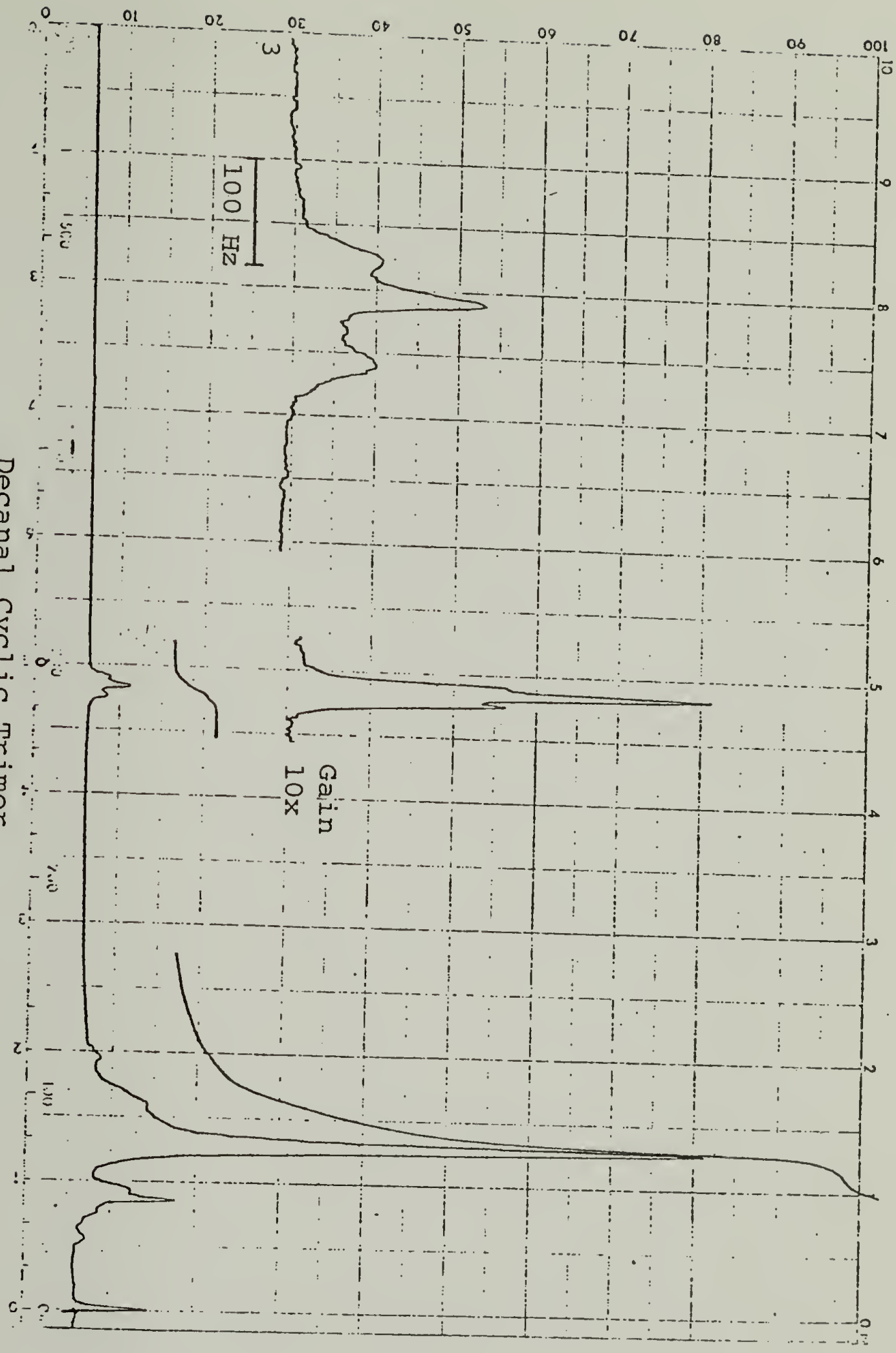

FREQUENCY (CM')
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
Polyundecanal-II
TRANSMITTANCE (%)
100
90
80
70
60
50
40
30
20
10
0
2.5
3.0
3.5
4.0
5
(MICRONS)
6
7
8
9
10
11
12
13
14
16
Dodecanal Polymerization
TRANSMITTANCE (%)
(MICRONS)

APPENDIX II

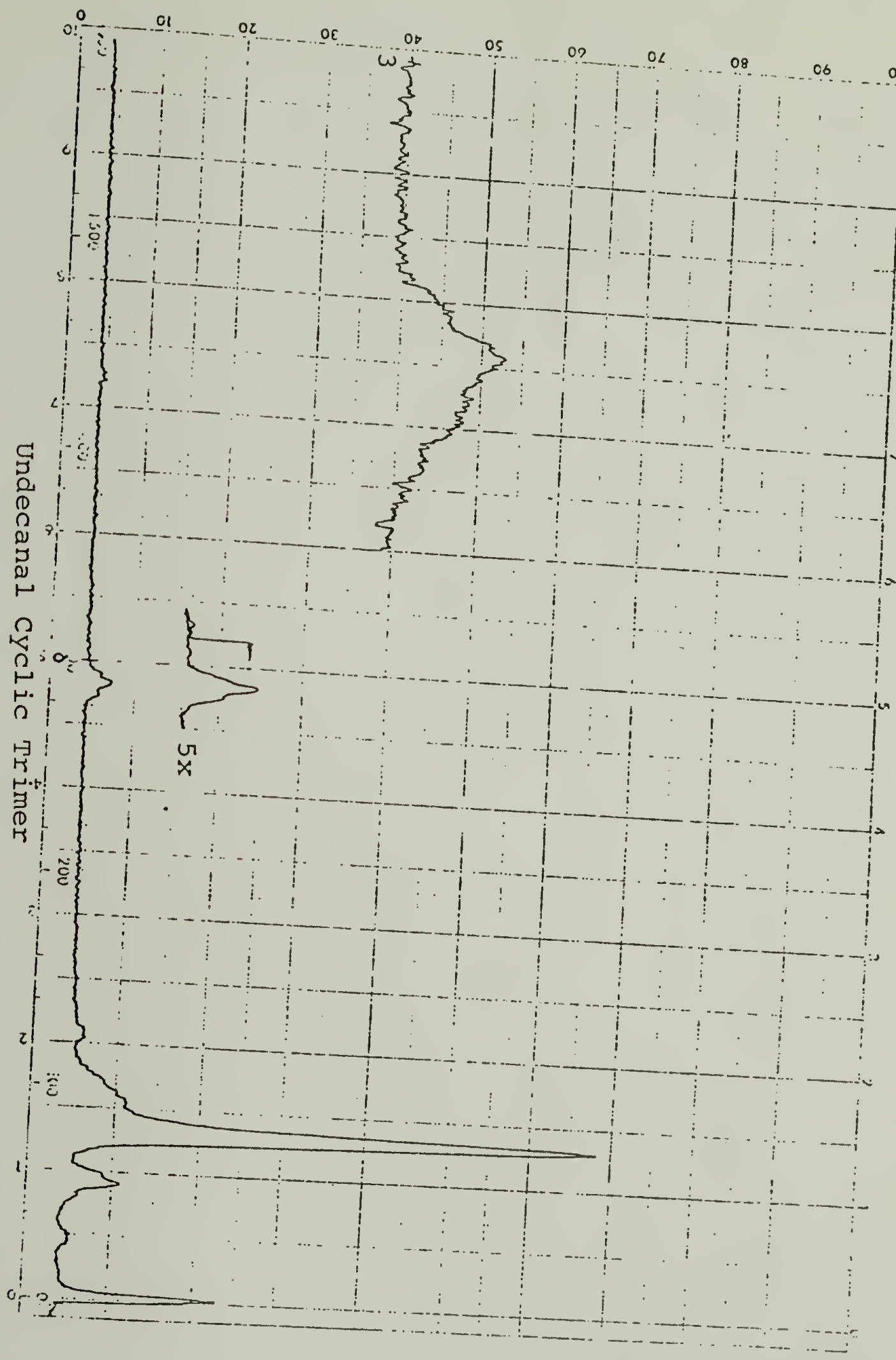
PMR SPECTRA



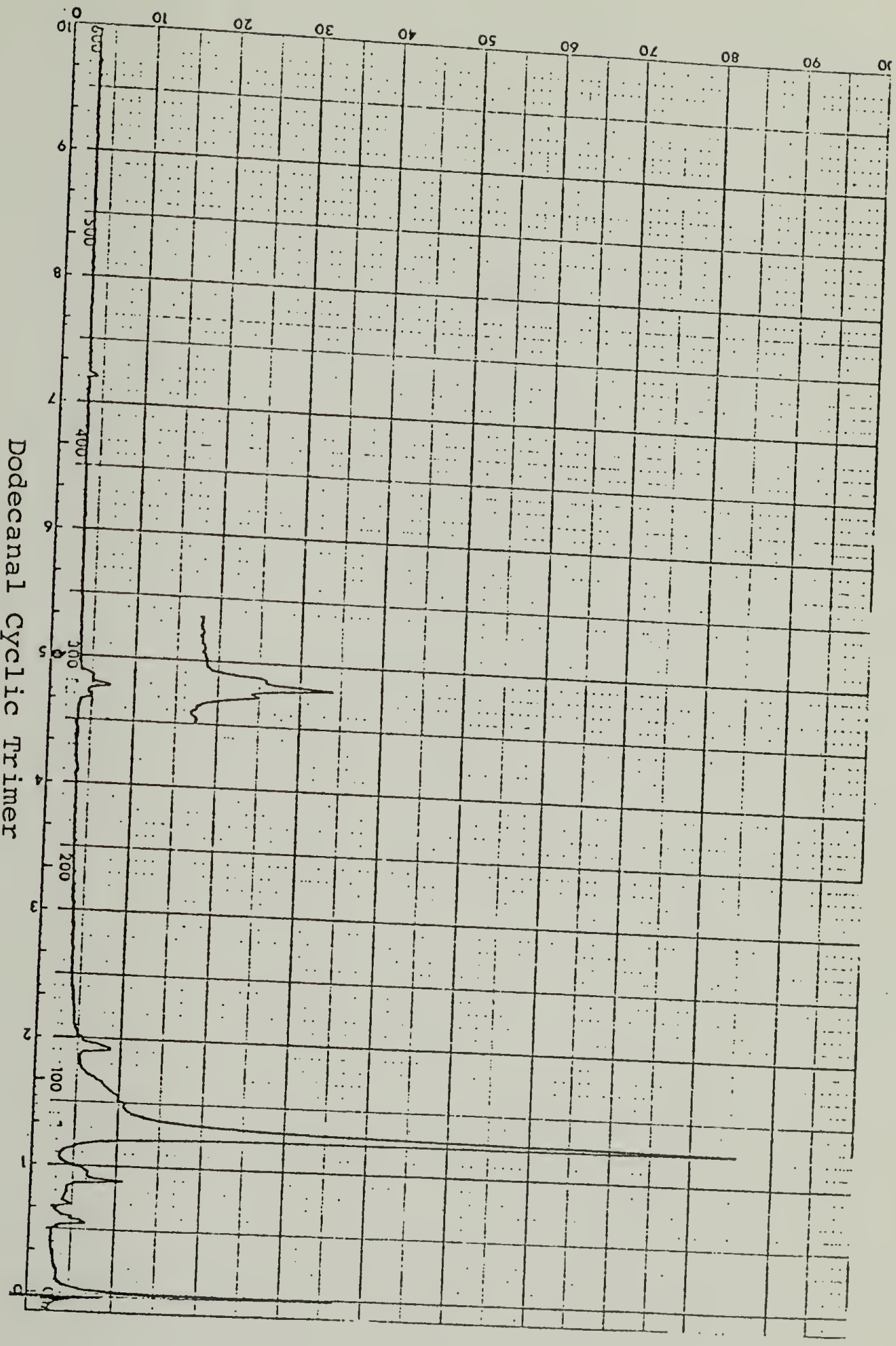
Nonanal Cyclic Trimer (H_2SO_4 catalyst)

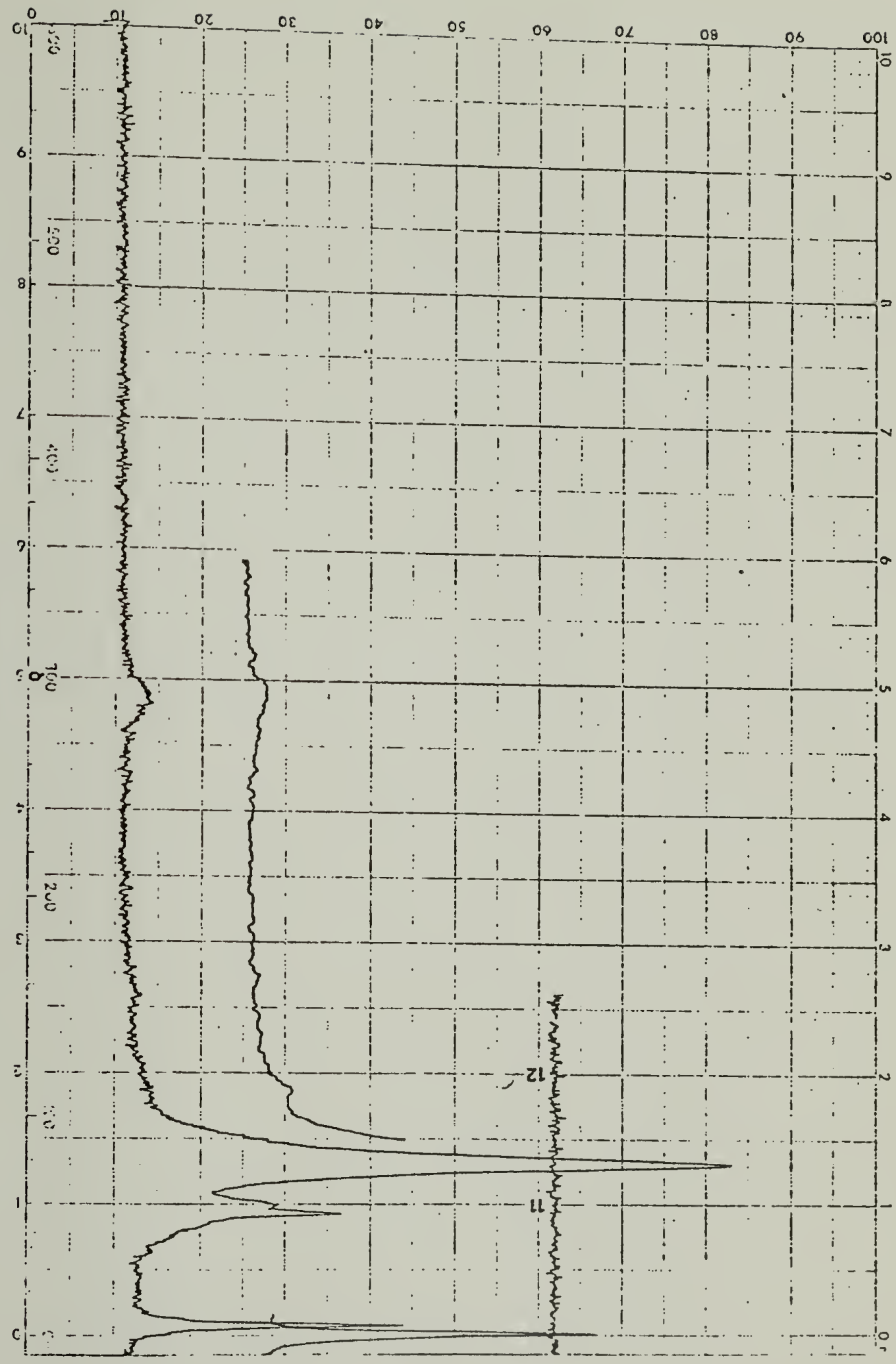


Decanal Cyclic Trimer

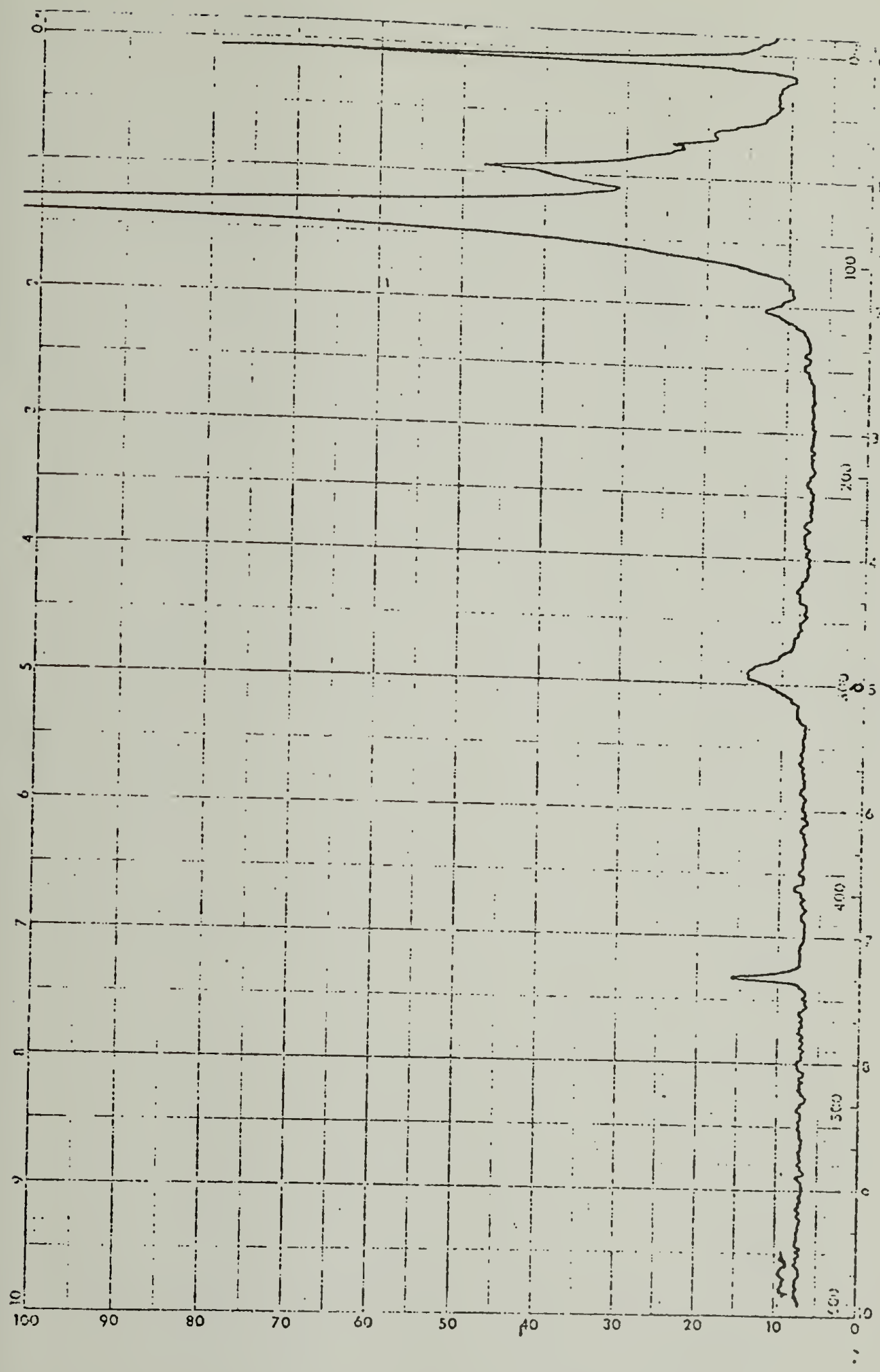


Undecanal Cyclic Trimer

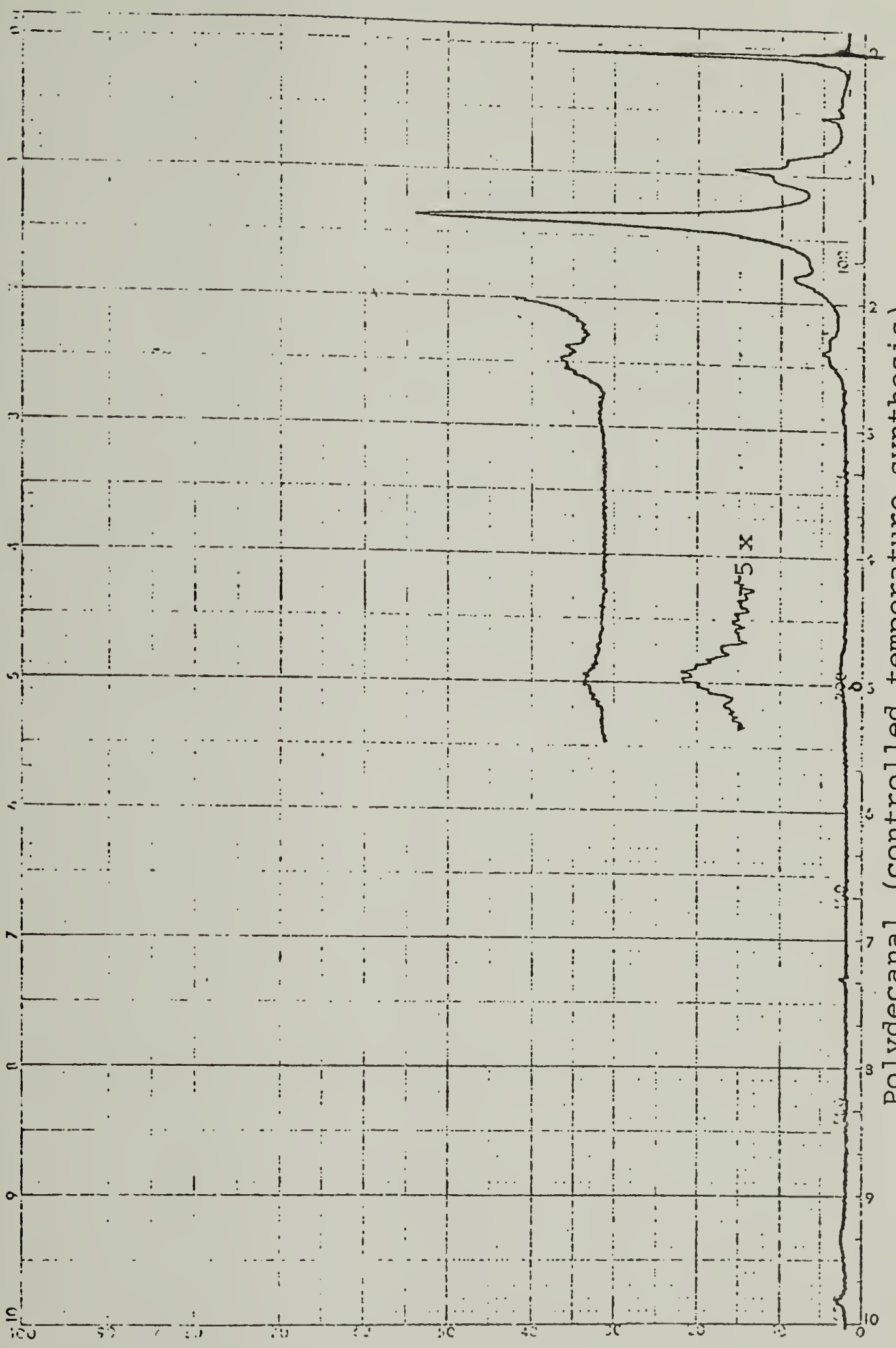

Dodecanal Cyclic Trimer
3000
2000
1500
1200
1000
900
800
700
600
500
400
300
200
100

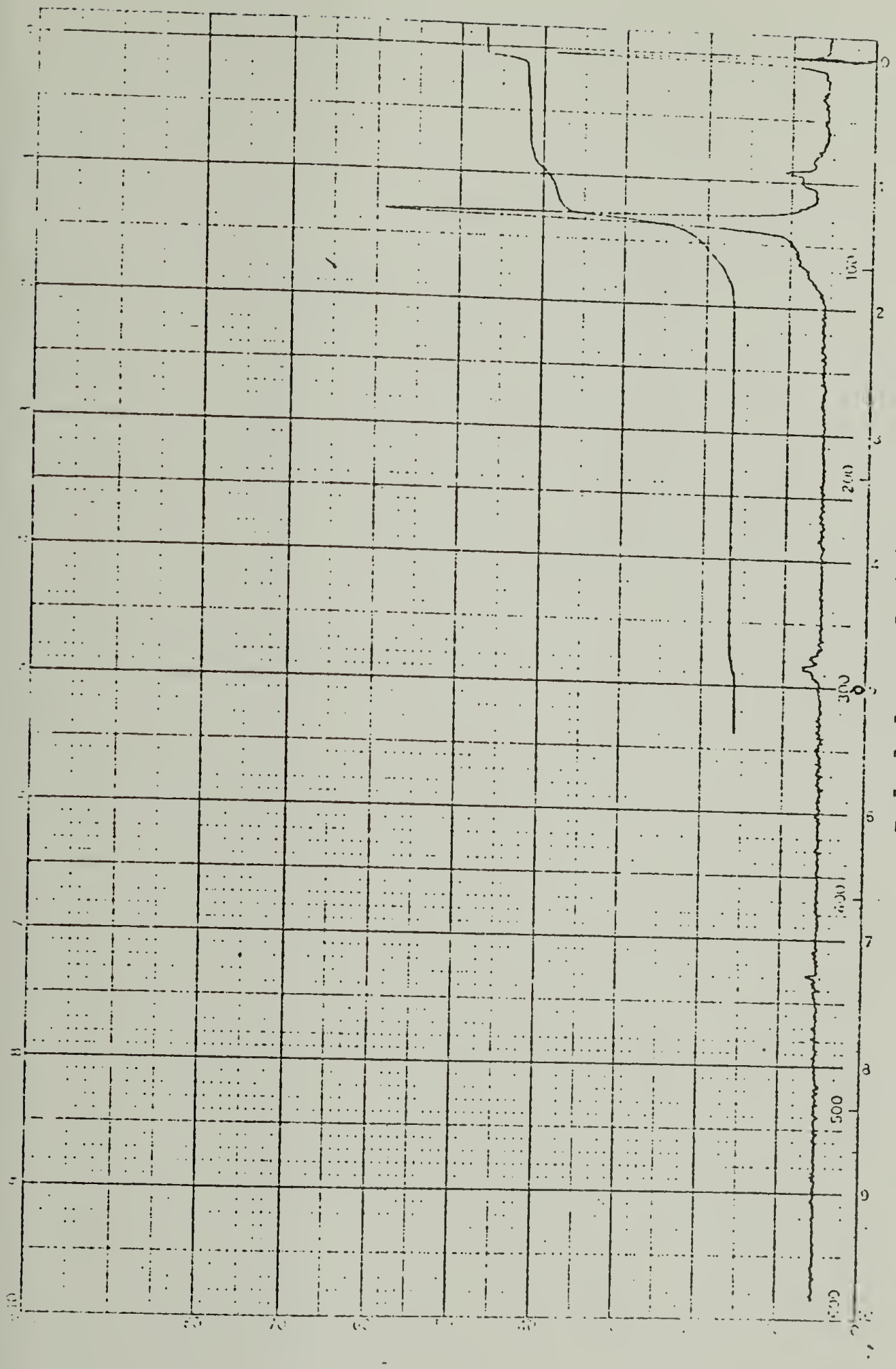


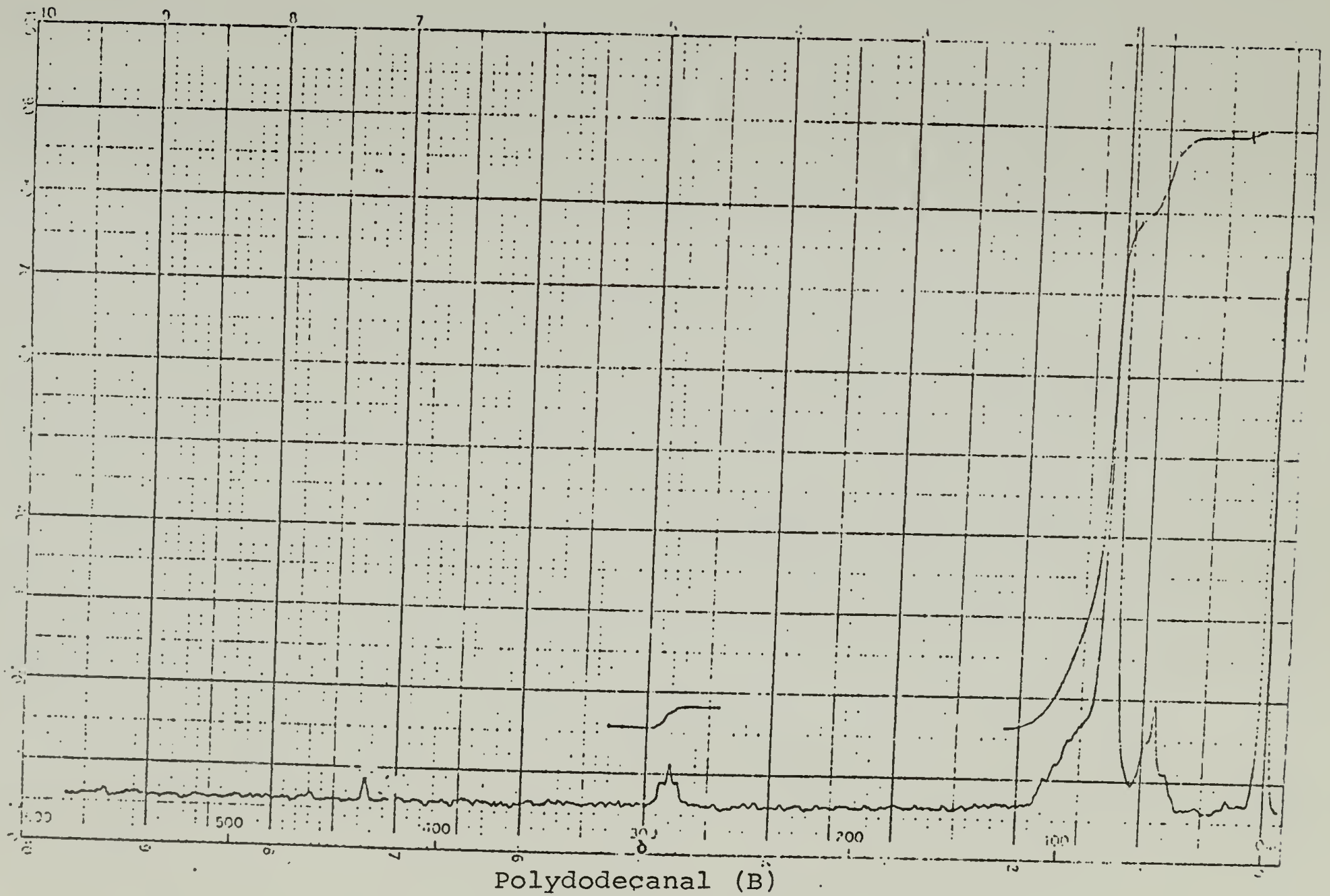
Polynonal



Polynonanal (controlled temperature synthesis)


x5
Polydecanal (controlled temperature synthesis)

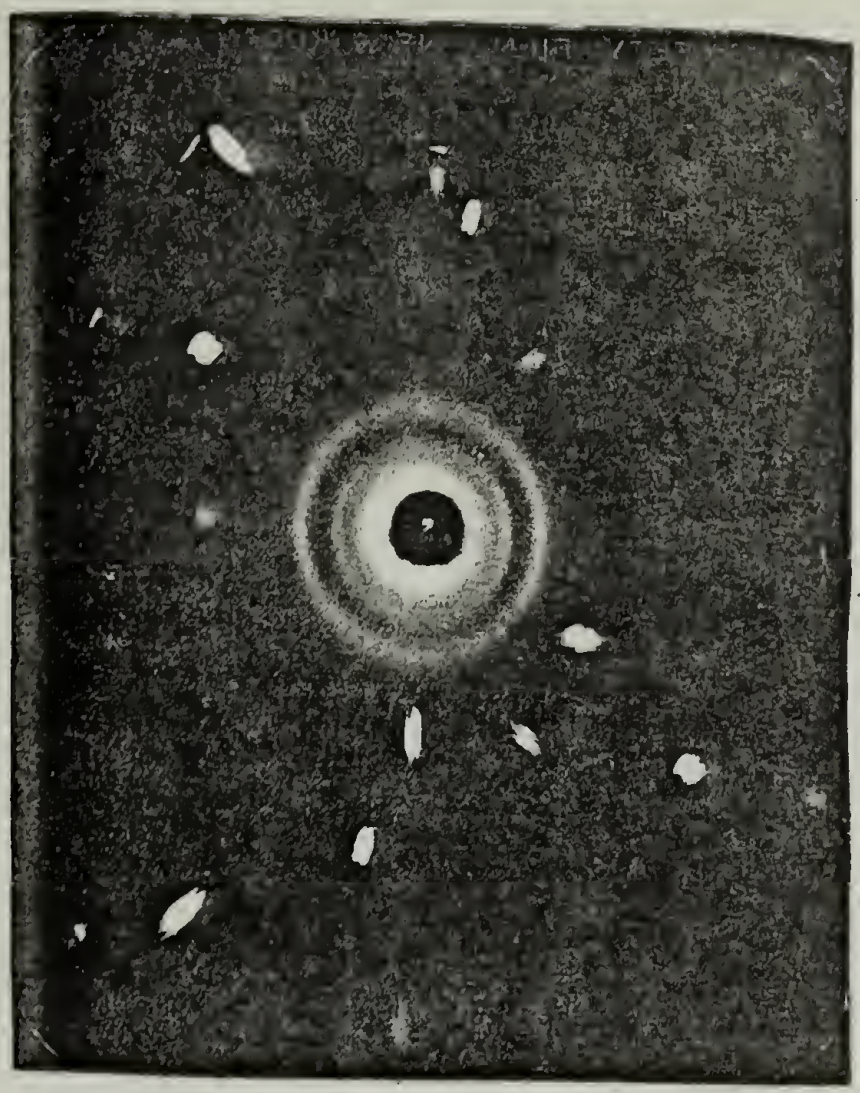

Polydodecanal (A)



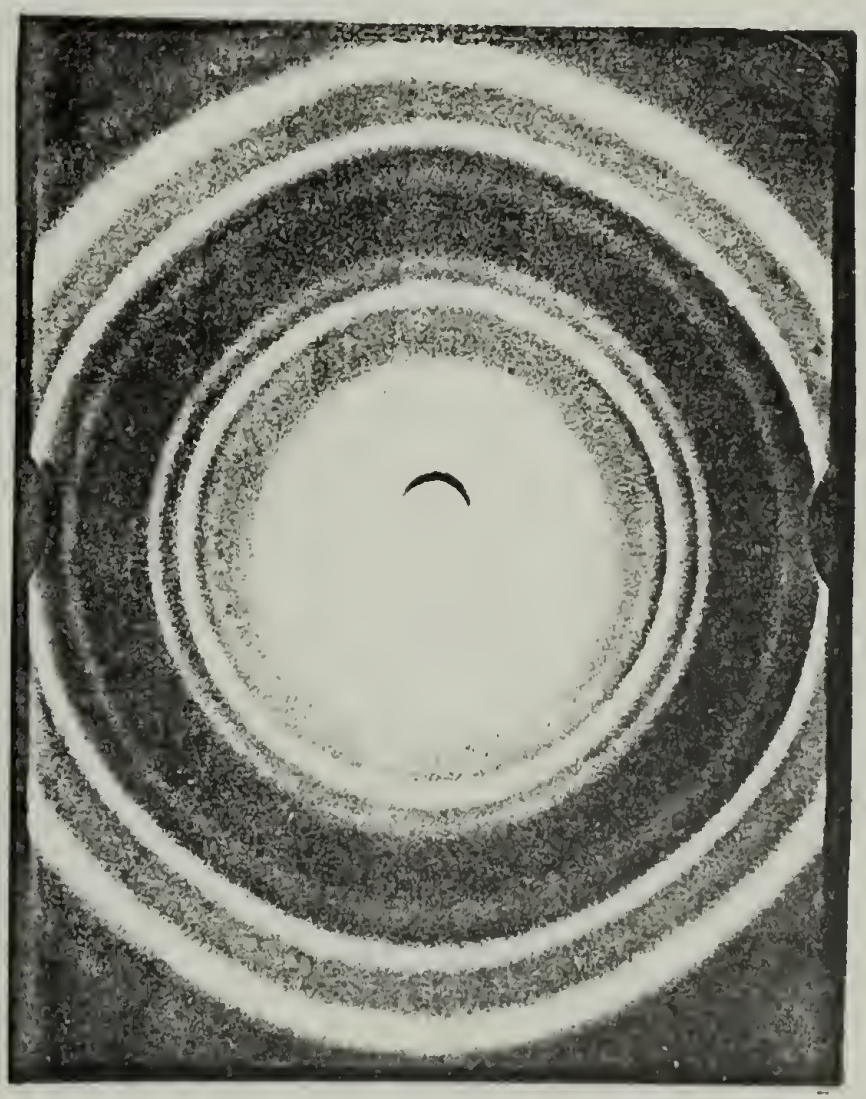
Polydodeçanal (B)

APPENDIX III

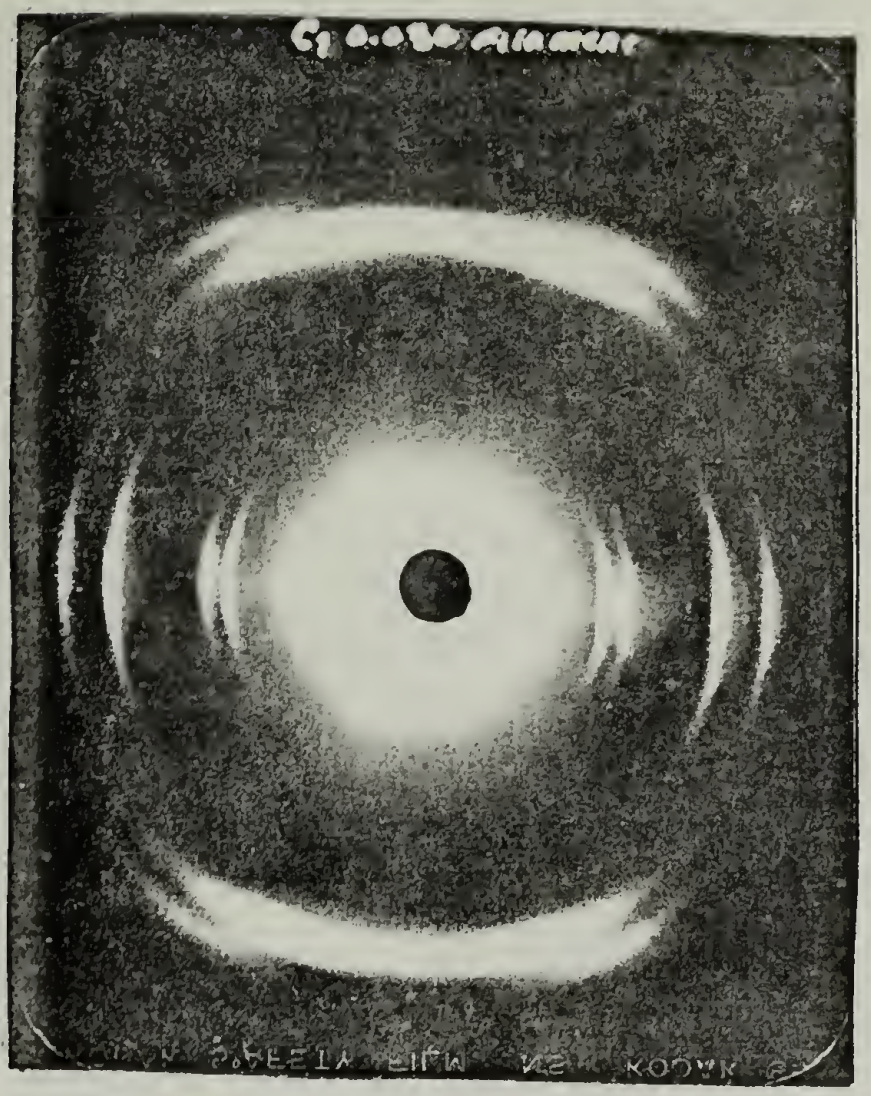
X-RAY DIAGRAMS



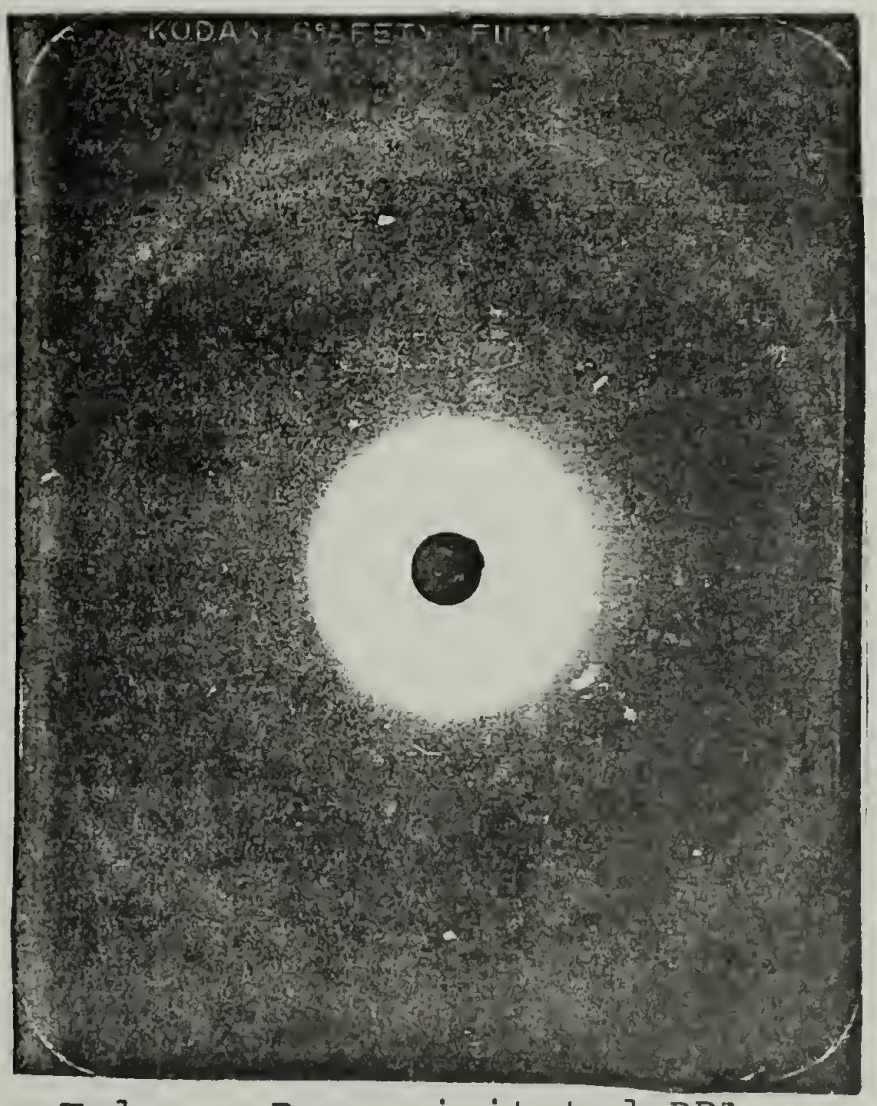
Toluene Reprecipitated PNA-II



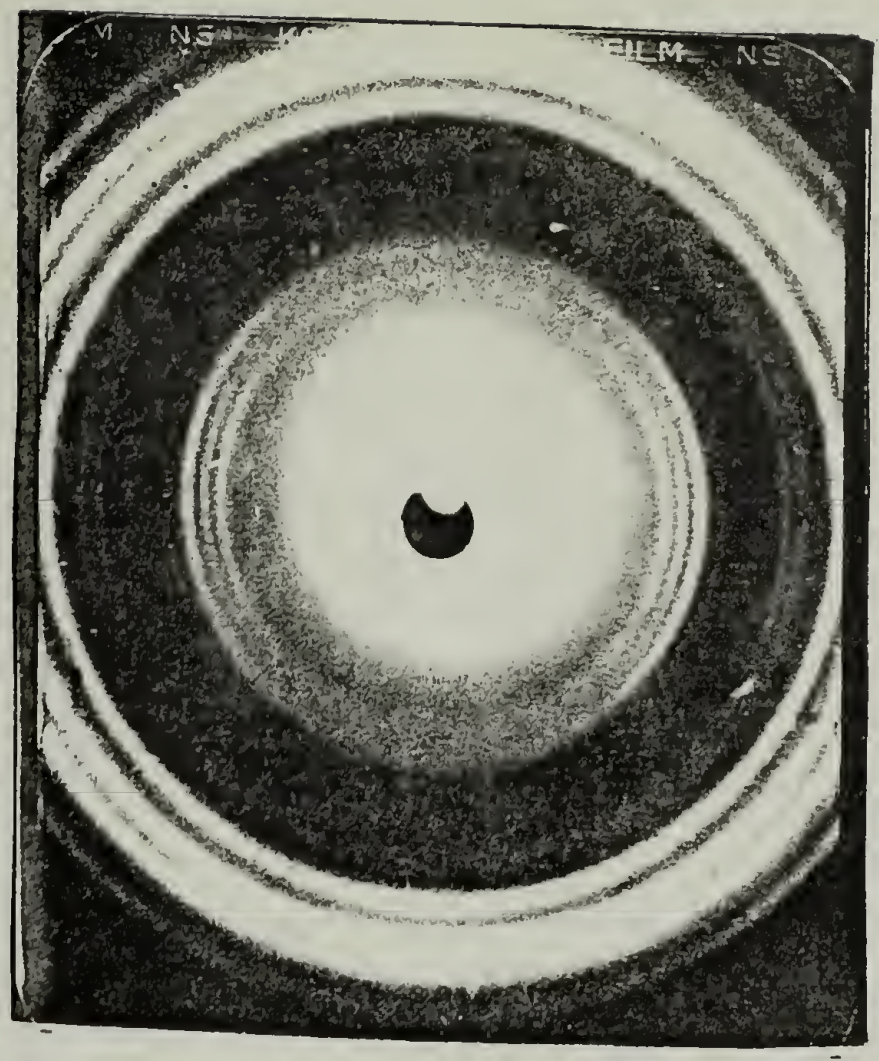
PNA-I



PNA-E

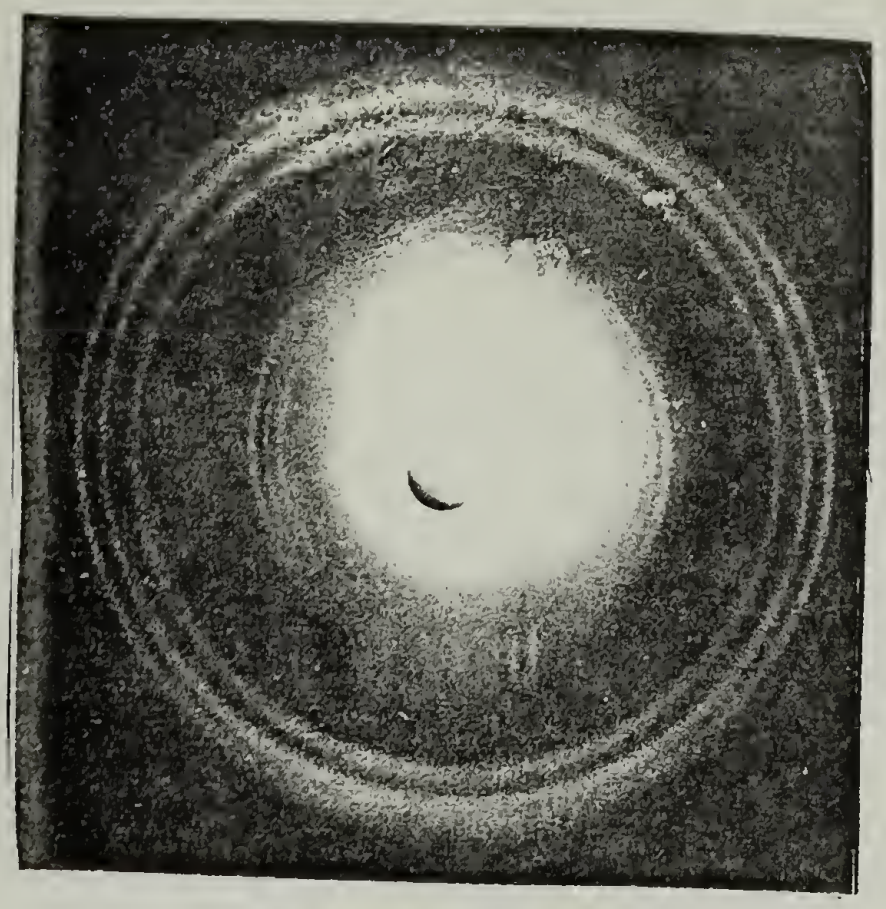


Toluene Reprecipitated PDA



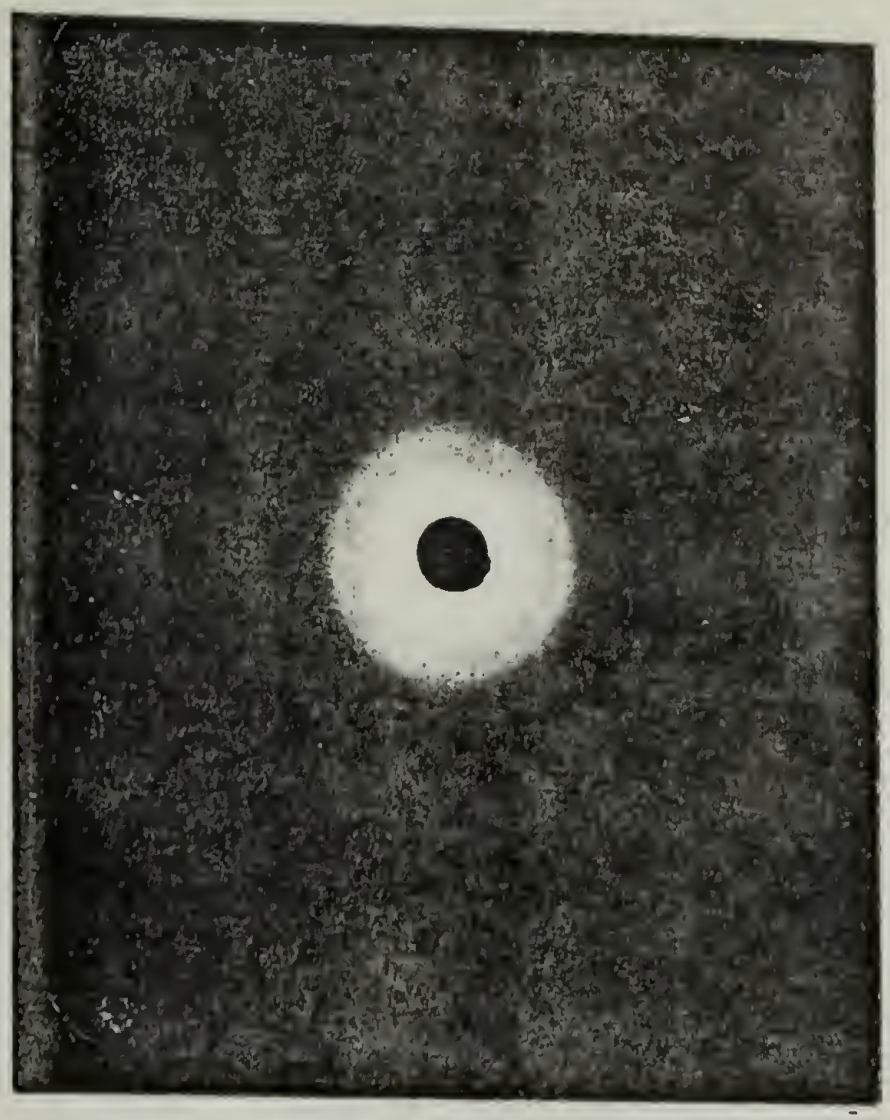
PDA First Extrusion 53°C, Exposure time, 14hr.

Reflection #	Relative Intensity	d (in Å)	Comments
1	m/s	27.14	
2	vs	14.19	may be two closely spaced reflections
3	m	8.40	
4	m	7.78	
5	m/s	7.24	
6	vw	6.78	
7	vw	6.43	
8	w	5.54	
9	w	5.27	
10	s	4.82	diffuse
11	s	4.45	diffuse
12	s	4.23	diffuse
13	m	3.90	
14	w	3.64	

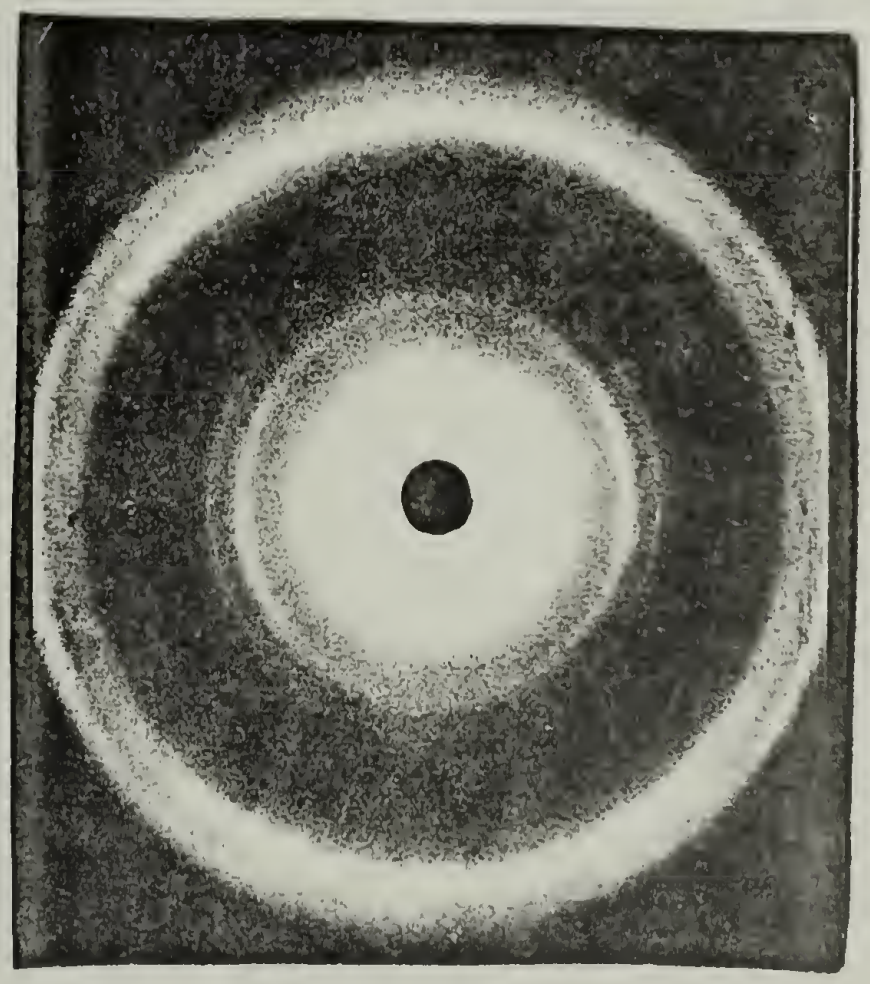


PDA Second Extrusion, 60°C. Exposure time, 14hr.

Reflection #	Relative Intensity	d (in Å)	Comments
1	vs	14.75	
2	m/w	8.71	
3	m	7.85	
4	m	7.32	
5	vw	6.74	
6	w	5.58	
7	w	5.23	
8	m/s	4.84	
9	m	4.45	
10	m/s	4.19	smeared in meridonal regions
11	w	4.00	
12	m	3.87	
13	vw	3.63	diffuse in all regions



PUA-I



PUA-II Extruded

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